# The Photochemical Reaction of Cycloöctatetraene ($C_8H_8$)

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## Introduction

The properties of cycloöctatetraene (C. O. T.) have been lately investigated by several physicochemical methods. We have calculated the energy levels of C.O.T. as the symmetry of $D_{2d}$,[1] $D_{4}$,[2] and $D_{4d}$[3] by the HLSP method[4] and the GMS method,[5] and then its electronic structure has been discussed in comparison with the experimental results of thermochemical data[6], magnetic susceptibility[7] and absorption spectra.[8]

We have newly found that C. O. T. undergoes the photochemical reactions by the mercury vapor lamp. Hence, C. O. T. was excited by mercury lamp and the gaseous products were examined by their absorption spectra. The quantum yield for benzene in the product was spectrographically determined, and the increase in the pressure of non-condensable producing gas was measured by a Bourdon gauge. The purpose of the present paper is to report these experimental results.

## Electronic Structure of C. O. T.

The energy levels of C. O. T. was calculated as the most probable symmetry of $D_{2d}$ by the HLSP method and the GMS method and are

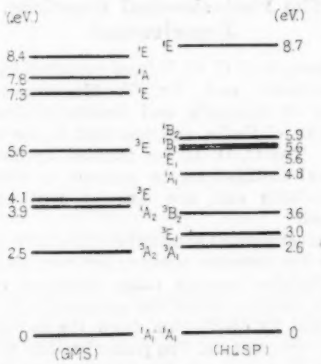


Fig. 1.

shown in Fig. 1. The absorption band below 2000 Å. was ascribed to the $^1A_1 \rightarrow {}^1E$ transition and the shoulder at 2800 Å. of the absorption band of longer wave length to the $^1A_1 \rightarrow {}^1A_1$ or $^1A_1 \rightarrow {}^1A_2$ transition. The levels which are calculated by the HLSP method for non-polar structures do not include the $^1A_2$ level. But the $^1A_2$ level appears in the calculation when it is only polar structures. The wave length of the transition $^1A_1 \rightarrow {}^1A_2$ is calculated to be shorter than 2000 Å. according to Craig's estimation.[9] But it is of interest as the property of approximate calculations that the levels appear on the lower or upper side; the molecular orbital introduces extra polar structures like GMS methods and makes the energy $^1A_2$ lower, while the atomic orbital raises the level $^1A_2$ made of polar structures.

There are some recent investigations about the interaction in the systems consisting of $I_2$ and aromatic compounds, especially benzene.[10] The following results were recognized from the relation obtained in the systems of $I_2$ and $C_8H_8$,[11] namely, the absorption band at 2800 Å. for $C_8H_8$ ($CCl_4$ solution + $I_2$) has the order of $\varepsilon = 450$, which is about twice as large as that of heptane solution ($\varepsilon = 250$), but does not

(1) H. S. Kaufmann, I. Fankuchen and H. Mark, *J. Chem. Phys.* **15**, 414 (1947); H. S. Kaufmann, I. Fankuchen and H. Mark, *Nature*, **161**, 165 (1948); K. Hedberg and V. Schomaker, Annual Meeting of Am. Chem. Soc., 1949.

(2) E. P. Lippincott, R. C. Lord and R. S. MacDonald, *J. Chem. Phys.* **16**, 548 (1948); E. P. Lippincott, R. C. Lord and R. S. MacDonald, *Nature*, **166**, 227 (1950); O. Bastiaisen and O. Hassel, Acta Scandinavica, **3**, 209 (1949).

(3) O. Bastiaisen, O. Hassel and A. Langseth, *Nature*, **169**, 128 (1947); B. D. Saksena and H. Narain, *Nature*, **165**, 723 (1950).

(4) I. Tanaka and S. Shida, This Bulletin, **23**, 54 (1950).

(5) Y. Mori, I. Tanaka and S. Shida, *ibid.*, **23** 168 (1950).

(6) D. W. Scott, M. E. Gross, G. D. Oliver and H. M. Huffmann, *J. Am. Chem. Soc.*, **71**, 1634 (1949); E. J. Prosen, W. H. Johnson and F. D. Rossini, *J. Am. Chem. Soc.* **69**, 2068 (1947); E. J. Prosen, W. H. Johnson and F. D. Rossini, *J. Am. Chem. Soc.* **72**, 626 (1950); J. L. Cotrell and L. E. Sutton, *J. Chem. Phys.* **15**, 685 (1947).

(7) R. C. Pink and A. R. Ubbelohde, *Nature*, **160**, 502 (1947); R. C. Pink and A. R. Ubbelohde, *Trans. Faraday Soc.*, **44**, 708 (1948); F. R. M. MacDonnell, R. C. Pink and A. R. Ubbelohde, *Trans. Faraday Soc.*, **46**, 156 (1950); S. Shida and S. Fujii, Annual Meeting of Chem. Soc. Japan, 1950.

(8) A. Langseth and S. Broderson, *Acta Chemica Scandinavica*, **3**, 778 (1949); S. Miyakawa, I. Tanaka and T. Uémura, in process of publication.

(9) D. P. Craig, Proc. Roy. Soc., **A 200**, 272, 390, 401 (1950).

(10) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71** 2703 (1949); R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 600 (1950).

(11) unpulished.

increase more than fifty times as in the case of benzene. So it is concluded that the electronic structure of C. O. T., though it being a ring compound, is different from those of the aromatic compounds. This conclusion coincides with the experimental results of the previous reference papers.[1]~[8], [12]

## The Photochemical Reactions, Experimental

The sample of C. O. T. was prepared by Prof. S. Murahashi and Dr. N. Hagiwara in the Institute of Scientific and Industrial Research, University of Osaka and was used in our experiments. The C. O. T. was purified by four time fractional distillations in vacuum in which the more volatile and the heavier portions were discarded.

The experimental arrangement is shown in Fig. 2. The low pressure mercury arc was set against the cylindrical quartz tubes (reaction cell) of different lengths, where the gaseous C. O. T. was introduced by distillation from the sample tube at room temperature. The photochemical reactions of C. O. T. in the cell were carried out by light which passed a filter between the cell and the arc. On the other hand, another cell with plane quartz windows was set between Jobin-Yvon spectrograph and the hydrogen discharge tube that was connected with the first cell so that the gaseous C. O. T. and its products diffuse into the cell. Their absorption spectra could thus be obtained.

The quantum yield of the reaction where C. O. T. is decomposed into benzene was determined using the uranyl sulfate and oxalic acid as actinometer. Corrections were made for light reflection on quartz-air interfaces.

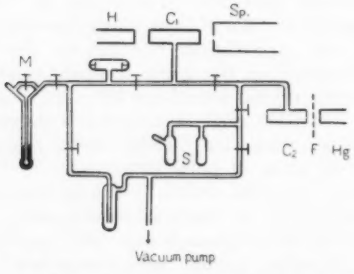


Fig. 2.—M, manometer; H, hydrogen discharge tube; $C_1$ and $C_2$, cell; Sp, spectrograph; S, sample; F, filter; and Hg, mercury lamp.

We have found the benzene as a product, hence the following process can be considered, $C_8H_6 + h\nu \rightarrow C_6H_6 + C_2H_2$. If this mechanism is true, it is expected that the pressure should increase as a result of the formation of $C_2H_2$, non-condensed at low temperature. In order to ascertain this consideration, a cylindrical quartz cell of 20 cc. capacity was connected directly to a gauge of the Bourdon type and the pressure change of non-condensable gas can be read with a cathetometer.

These experiments were carried out in the pressure range from 2 to 7 mm.Hg. of C. O. T.. For the filter, glass (above 3300 Å.), P. V. A. (above 2300 Å.), etc. were used.

## Results and Discussions

First of all, the results which were qualitatively observed by the absorption spectra of photochemical products of C. O. T. are shown as follows. The characteristic absorption bands of benzene (2610 Å., 2550 Å., 2480 Å., 2420 Å., ....) were observed in the spectra which could be obtained through the second cell of 50 to 95 mm. length, by illumination of mercury arc, for 10 to 60 minutes. In order to find other substances but benzene, by using the second cell of 200 mm. length, narrowing the slit and operating the mercury arc for 1 to 3 hours, new absorption bands which were not recognized in the case of the shorter cell, could be found at 2916 Å. (s), 2916 Å.~2885 Å (diffuse), 2885 Å. (s), 2877 Å. (w), 2872 Å. (w), 2840 Å. ~2700 Å. (diffuse), 2816 Å. (w) and 2800 Å. (w) (where the notation s means strong and w weak intensity).

In order to study what substances have given these absorption bands, the absorption spectra of pure gaseous styrene were taken. Its strong absorptions at 2885 Å., 2877 Å., 2872 Å., 2816 Å. and 2800 Å. could be confirmed to coincide with the above-mentioned bands, so we can conclude that the styrene, an isomer of C. O. T., is also produced in the photochemical reaction of C. O. T. We can not yet determine from which of reacting substances come those bands at 2916 Å. (s), 2916 Å.~2885 Å. (diffuse band) and 2840 Å.~2700 Å. (diffuse band) which are not observed in the spectra of styrene. We may, however, suppose that these bands may be dependent on some compounds like C. O. T. which contain some conjugated double bonds, since these substances will have absorption bands of longer wave lengths than 2000 Å. In order to determine whether benzene can be directly produced by the photodecomposition of C. O. T. or by the photodecomposition of styrene that is produced by the isomerization of C. O. T., the reaction products, which were produced from pure styrene in gaseous phase by the mercury lamp at the same condition as the case of the photoreaction of C. O. T., can be studied their absorption spectra. The reactions by the illuminations for 10 min., 30 min., and 60 min. gave no benzene at all, and

(12) Cf. R. M. Elofson, *Anal. Chem.*, **21**. 917 (1949).

the intensity of the absorption spectra of styrene was only decreased. This fact is probably due to the photopolymerization of styrene. So that, we can ascertain that the photodecomposition to benzene is the direct one.[13]

If we compare the absorption spectra which were obtained in 200 mm. cell for the resultant of the photochemical reaction and the spectra that were respectively obtained from pure styrene in various pressures, we can recognize that the quantity of reaction of photodecomposing to benzene is larger than that of isomerizing to styrene, although this conclusion is not certain, because the styrene changes to polystyrene in small quantity.

It may be considered that the reason why the photodecomposition of C. O. T. to benzene is easier than the isomerization of C. O. T. to styrene is that after the excitation by photon the breaking of the single bonds (=CH–CH=) is easier than the displacement of the hydrogen atom.[14]

Next, to investigate the reaction $C_8H_8+h\nu\rightarrow C_6H_6+C_2H_2$, the results that are obtained for the non-condensable gas at low temperature will be illustrated. A trap which is prepared between the cylindrical quartz cell (20 cc.) and Bourdon Gauge, can be cooled after the exposition of the cell to light, in alcohol with dry ice to condense out C. O. T., benzene, styrene, and etc., and the pressure of non-condensable gas could be measured. The initial pressure of C. O. T. was 2.50 to 3.50 mm.Hg. An example is shown in Table 1.

Table 1

| The initial pressure of C. O. T., mm.Hg | Filter | Pressure of non-condensable gas, mm.Hg | | |
|---|---|---|---|---|
| | | 10 min. | 30 min. | 60 min. |
| 2.60 | None | 0.06 | 0.14 | 0.25 |
| 2.92 | P. V. A. | — | 0.04 | 0.06 |
| 3.32 | Glass | 0 | 0 | 0 |

Conditions of above reaction: The cell is set parallel to mercury arc. (100 V., 5 Amp.) Temp. 25°.

The measured values of transmissions of the filters used are shown in Fig. 3. According to these results that are given in Table 1, it is clear that besides $C_6H_6$ a non-condensable gas, probably $C_2H_2$, is produced by the photochemical reaction. When the light below 3300 Å. was cut off by glass, C. O. T. did not decompose photochemically as well as the results of quantum yield of $C_6H_6$ as stated later will show. By comparing the reactions with and without filter P. V. A. it is clear that the light below 2500 Å is important for the photochemical decomposition.

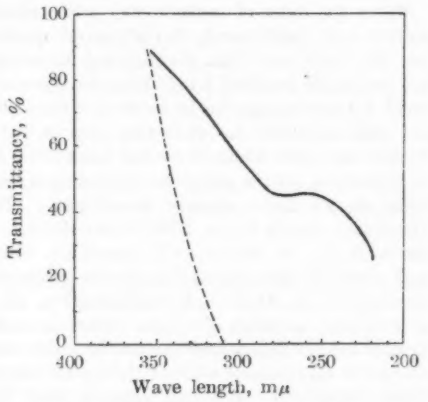


Fig. 3.—Transmission of the filters: ——, PVA-filter; – – –, glass.

Next, the quantum yield of reaction in which C. O. T. decomposes to benzene will be stated. The experimental arrangements are shown in Fig. 2.

In order to determine the quantity of benzene which is produced in the photochemical reaction, the extinction of pure benzene was first measured in various pressures by the microphotometry of the absorption spectra of gaseous benzene that were distilled three times in vacuum. The benzene which is produced by photochemical reaction in various conditions could be quantiatively determined. On the other hand, when we can measure the fraction of light that was absorbed by chemical actinometer, the quantum yield may be determined. An example of the experimental data is written in Table 2.

Table 2

The Photodecomposition of C. O. T. at 25°.

| The initial pressure of C. O. T., mm. Hg | Filter | Pressure of benzene produced, mm. Hg | | |
|---|---|---|---|---|
| | | 10 min. | 30 min. | 60 min. |
| 5.0 | None | 0.18 | 0.47 | 0.70 |
| 5.0 | P. V. A. | — | 0.13 | 0.23 |
| 5.0 | Glass | 0 | 0 | 0 |

(13) B. L. Dunicz, *J. Am. Chem. Soc.*, **63**, 2461 (1941). It was reported that the characteristic bands of styrene was not found in the course of the photochemical reaction in acetylene-benzene mixture for irradiation. The authors are indebted to Z. Kuri for valuable discussions about this experiment.

(14) Norrish, *Trans. Faraday* Soc., **30**, 103 (1934); Saltmarsh and Norrish, *J. Chem. Soc.*, 455 (1935); The interesting facts for shift of hydrogen atom about the photodecomposition of cycloketones were reported.

From the data of actinometry with uranyl sulfate and oxalic acid, the absorbed quanta are $5.1\times10^{18}$ and the decomposed molecules are $0.41\times10^{18}$ in a half hour. Then the quantum yield for decomposition to benzene is about 0.1 for light near 2537 Å. It is also seen in Table 2 that the light which is shorter than 2500 Å. is important for the photochemical decomposition, as we have already mentioned. The absorption bands below 2500 Å. can be considered as due to the $^1A_1\rightarrow{}^1E$ transition which was given by the calculation for the electronic structure of C. O. T. A configuration of a polyatomic molecule for an electronic state having orbital degeneracy can not be stable with respect to all displacements of the nuclei (Jahn-Teller effect).[15] We can suppose that the Jahn-Teller effect will be very small in benzene, even if it occurs, as $\pi$-electrons have less contribution to the chemical binding than $\sigma$-electrons, then the decomposition is impossible by mercury lamp.[16] We may consider that C. O. T. is not stable through the change of the shape of molecule as the Jahn-Teller effect is more effective for C. O. T. than for benzene and C. O. T. will be decomposed by light which has shorter wave length than 3000 Å.

(15) H. A. Jahn and E. Teller, *Proc. Roy. Soc.*, **A 161**, 220 (1937); H. A. Jahn, *ibid.*, **A 164**, 117 (1938).
(16) Kistiakowsky and Solomon, *J. Chem. Phys.* **5**, 609 (1937).


## Summary

By the absorption spectra, it was found that benzene and styrene were independently produced from C. O. T. when C. O. T. was excited by the light shorter than 3000 Å., and that some unknown substances giving a sharp line at 2916 Å. and two diffuse bands at 2916 Å.~2885 Å. and 2840 Å.~2700 Å. were also produced. The gas like acetylene which can not be condensed by dry ice can be at the same time produced.

The quantum yield of reaction where C. O. T. is decomposed to benzene by light near 2537 Å. was about 0.1. And the light which has the shorter wave length than 2500 Å. mainly contributes to the reaction in which C. O. T. decomposes to benzene.


The authors deeply wish to express their appreciation to Prof. S. Murahashi and Dr. N. Hagiwara who have furnished them the C. O. T. and have also given many valuable advices and also to Prof. T. Uemura who has stimulated them. Authors' sincere thanks are also due to the Ministry of Education for the financial grant.

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# On the Etched Surfaces of Nickel Single Crystals Revealed by Means of Electron Diffraction and Microscopy

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The etched surfaces of nickel single crystals were here examined by means of electron diffraction and oxide replica of microscopy. The electron diffraction method identified the crystalline substances found in the etched surfaces of specimens and determined their crystallographic orientation. The oxide replica method of electron microscopy clarified the forms and orientation of the metal crystals on the etched surfaces of specimens. It was demonstrated in the present study that the combination of electron diffraction and microscopy made it possible to assign the crystallographic indices to the etched surfaces of single crystals of nickel. It is important to ascertain the particular crystallographic arrangement characteristic to the atoms on the etched surface, because the physical and chemical properties (*e. g.*, catalysis,[1] corrosion-resistance[2] *etc.*) of nickel crystal should be discussed in relation to the atomic arrangement experimentally determined.[3]

(1) O. Beeck, *Rev. Mod. Phys.*, **17**, 61 (1945).
(2) S. Yamaguchi, T. Nakayama and T. Katsurai, *J. Electrochem. Soc.*, **95**, 21 (1949).
(3) T. N. Rhodin, *J. Appl. Phys.*, **21**, 971 (1950).

## Experiments

The three types of nickel single crystals[4] employed in the present experiments were the three metal discs (diameter : 10 mm., thickness : 2 mm.) cut along the (001), (110) and (111) planes respectively. These specimens were named No. 1, 2 and 3 here. The surfaces of these three types of disc specimens were buffed and then etched with ethanol-bromine (10 : 1 by vol.) for 10-20 seconds. These specimens gave respectively different etching figures to naked eyes. These etched surfaces were observed at first by means of electron diffraction and then oxide replica method of electron microscopy.

The specimen No. 1 gave the diffraction patterns shown in Photos. 1-4. These diffraction patterns verified the existence of pure nickel crystal in the etched surface of specimen. Photo. 1 coincides with the diffraction pattern which should be given by the electron beam running parallel to the (001) and (110) planes of nickel single crystal. The electron beam in obtaining Photo. 1 was nearly parallel to the macroscopic surface of etched specimen. Photos. 2 and 3 were obtained from the specimen surfaces rotated respectively by 15° and 30° from the position of Photo. 1. Photo. 4 was obtained from the specimen whose macroscopic surface was inclined by 2° to the incident beam in the position of Photo. 2. These four diffraction patterns verified that the macroscopic etched surface of specimen No. 1 was approximately parallel to the (001) planes of nickel single crystal.

The etched surface giving the diffraction patterns of Photos. 1-4 was treated in an autoclave (water vapor pressure : 15-20 atm., duration of reaction: 5hrs.) in order to form the structureless oxide film on the specimen surface. This oxide film was stripped from the substrate by Mahla-Nielsen's method[5] with ethanol-bromine solution. The isolated film was magnified by means of electron microscopy. The electron micrograph obtained is shown in Photo. 5. It is seen in Photo. 5 that the crystals of cubic form (size: 30 mμ-300 mμ) are oriented in one direction. Some side planes of the single crystals recognized in Photo 5 are distinctively more opaque than the other planes. This means that the crystallographic indices for the opaque planes are different from those for transparent planes, since the former planes have been oxidized more deeply than the latter. It is, therefore, concluded in reference to the results of diffraction experiments described above that the etched surface of specimen No. 1 is composed of the (001) and (110) planes, as is shown in Fig. 1. It is surmised here that the (110) faces are more easily oxidized than the (001) planes.

The specimen No. 2 gave the diffraction patterns shown in Photos. 6-8. Many fine grooves arranged

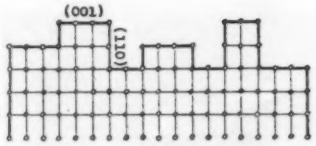


Fig. 1.—Profile of specimen No. 1 sectioned parallel to (1$\bar{1}$0) plane. Atom distances: 3.52 Å. and 2.49 Å.

parallel with each other were observed by naked eyes on the etched surface of the specimen. The electron beam running parallel to these grooves gave the diffraction shown in Photo. 6. The beam intersecting at the angles of 45° and 90° to the direction of the grooves gave the patterns of Photos. 7 and 8 respectively. These diffraction patterns verified that the macroscopic surface of specimen No. 2 was parallel to the (110) planes of nickel crystal and the direction of the grooves was parallel to the (1$\bar{1}$0) direction.

The etched surface of specimen No. 2 was magnified by means of electron microscopy, as is shown in Photo. 9. The long crystals oriented parallel to each other in Photo. 9 might be seen as etching grooves with naked eyes. In this way the profile of specimen No. 2 sectioned parallel to cube face was shown schematically in Fig. 2, *i.e.*, the etched surface of specimen No. 2 is composed of the (110) and (1$\bar{1}$0) planes.

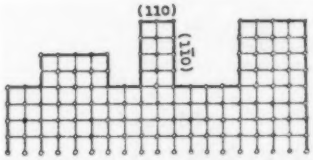


Fig. 2.—Profile of specimen No. 2 sectioned parallel to cube face. Atom distance: 2.49 Å.

Speccimen No. 3 gave the diffraction pattern of Photo. 10. The incident electron beam in Photo. 10 is parallel to the (111) and (1$\bar{1}$0) planes of nickel crystal. Since the incident beam was nearly parallel to the macroscopic surface of the etched specimen, the etched surface of the specimen was parallel to the (111) planes and perpendicular to the (1$\bar{1}$0) planes. The Kikuchi-lines are found in Photo. 10. This means that the etched surface of the specimen is rather flat than thorny.

The magnified reprints of the etched surface of specimen No. 3 are shown in Photos 11 and 12. There are many lamellar crystals of triangular form in Photos 11 and 12. The faces of the lamellae had to be assigned with (111) indices in reference to the results of the diffraction experiments. The surface of specimen No. 3 was composed of the (111) and (1$\bar{1}$0) planes, as is shown schematically in Figs. 3 and 4.

(4) These single crystals were prepared by S. Kaya, and J. Horiuti used these crystals for the samples in the experiments on chemical kinetics.

(5) E. M. Mahla and N. A. Nielsen, *J. Appl. Phys.*, **19**, 378 (1948).

Fig. 3.—An exaggerated sketch of Photo 11.

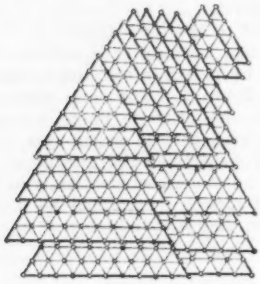

Fig. 4.—Projection of the etched surface of specimen No. 3 showing the (111) faces. Atom distances, 2.49 Å.

## Discussion

The crystallographic assignment of the boundary planes of the powder crystals was able to be carried out by means of electron microscopy and microscopic diffraction.[6] In order to assign crystallographically the boundary planes of bulk single crystal, however, it was necessary to rely on the oxide replica method and the electron reflection method of diffraction as given in the present study.

The temper colors obtained on the etched surfaces of the specimens on exposure to the air were here observed. The etched surface of specimen No. 2, which was composed of the (110) and $(1\bar{1}0)$ faces, became mat rapidly in the air at room temperature. On the other hand, the etched surface of specimen No. 3, which was composed of the (111) and (110) faces, became mat very slowly in the air at room temperature. These facts indicated that the (110) face, whose atomic arragement is coarse, is chemically most active, and the (111) face, which consists of the closest packed atoms, is most inert among the principal faces of nickel crystal.

## Summary

(1) It was possible to assign the crystallographic indices to the etched surfaces of single crystals by the combination of electron microscopy and diffraction.

(2) The (110) plane of nickel crystal was most active and the (111) plane was most inactive among the principal planes of crystal.

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(6) A. C. Dorsten, H. Nieudorp and A. Verhoeff, *Philips Tech. Rev.*, **12**, 33 (1950).

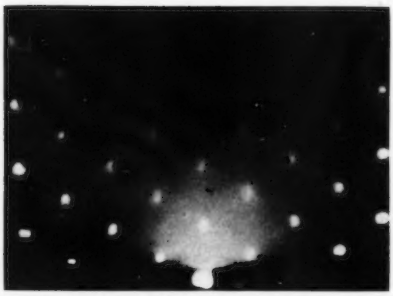

Photo. 1.—Incident beam is parallel to (001) and (110) planes. Macroscopic surface is parallel to (001) planes.

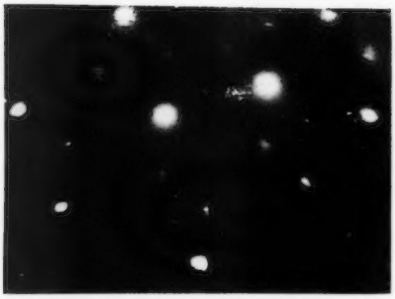

Photo. 2.—Diffraction from the specimen surface rotated by 15° from the position of Photo. 1.

Photo. 3.—Diffraction from the specimen surface rotated by 30° from the position of Photo. 1.

Photo. 4.—Diffraction from the specimen surface inclined by 2° to incident beam in the position of Photo. 2.

Photo. 6.—Diffraction of the incident beam parallel to the etching grooves of specimen No. 2.

Photo. 7.—Diffraction from the specimen surface rotated by 45° from the position of Photo. 6.

Photo. 8.—Diffraction from the specimen surface rotated by 90° from the position of Photo. 6.

Photo. 10.—Diffraction from the etched surface of specimen No. 3. Macroscopic surface of specimen is parallel to (111) planes

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Photo. 5.—Electron micrograph of the etched surface of specimen No. 1.

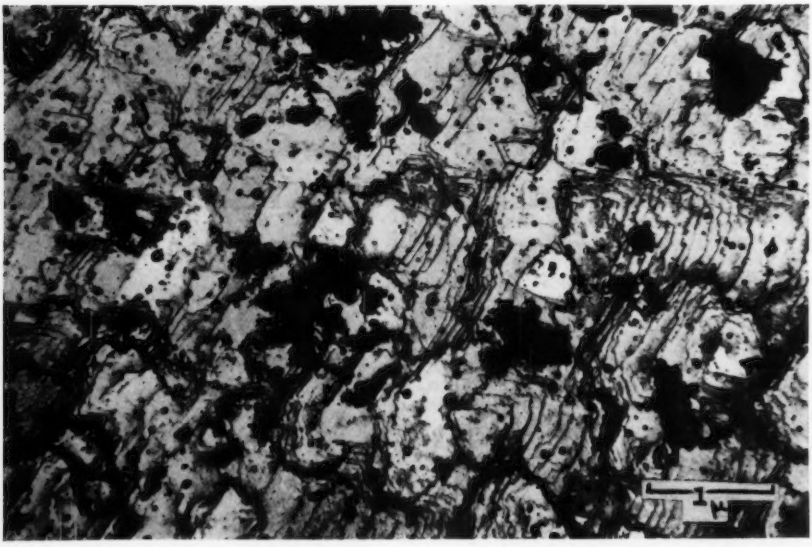


Photo. 11.—Electron micrograph of the etched surface of specimen No. 3. There are many lamellar crystals.

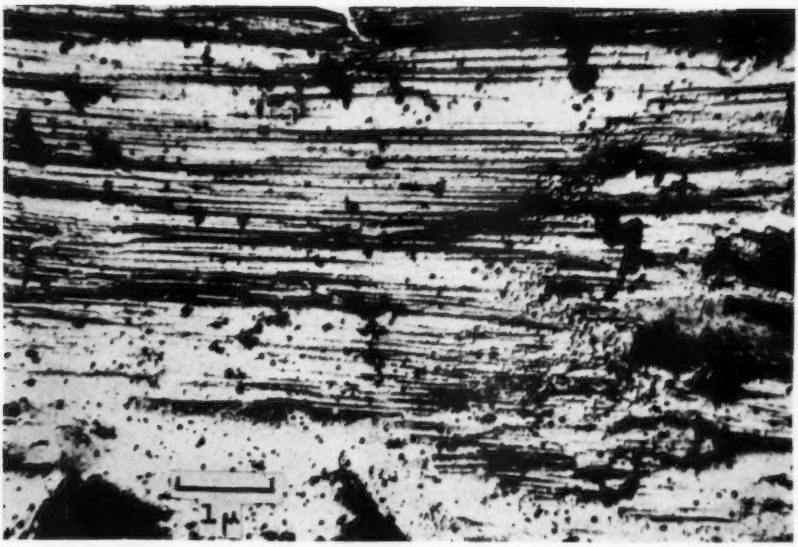


Photo. 9.—Electron micrographs showing etching grooves on the surface of specimen No. 2.

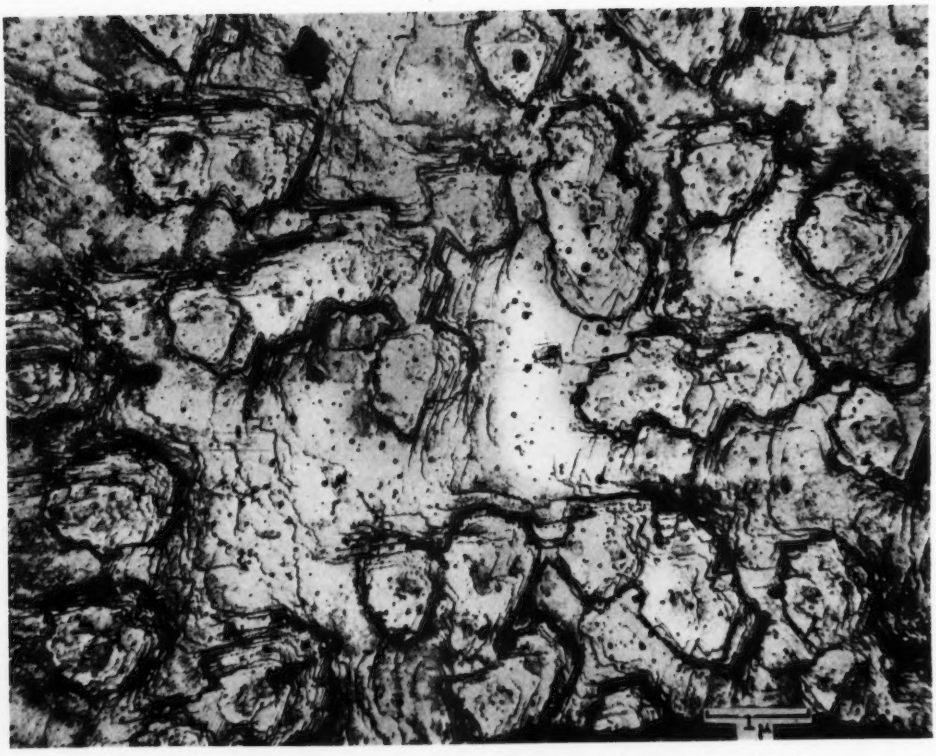


Photo. 12.—Electron micrograph of the etched surface of specimen No. 3. There are lamellae of triangular form.

# Researches on Dichroism of Planar Complexes. III. The Color and the Structure of the Crystals of Tetracyanoplatinates (II)

By Shoichiro YAMADA

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Crystals of some tetracyanoplatinates (II) have been known to show unusually deep colors. For example, crystals of the barium and calcium salts are yellow, and those of the magnesium salt orange red; they show different colors for different degrees of hydration of the same cations, whose aqueous solutions are all colorless. Such unusual colors of the salts, which seem closely related to the anisotropic character of the planar tetracyanoplatinates (II), indicate that planar complexes in these crystals are in a condition quite different from their state in solution. On the colored crystals of tetracyanoplatinates (II) there have been reported several researches, which, however, have scarcely dealt with the relation between absorption and structure or bonding; nor has any plausible explanation as to the colors of the crystals of these compounds been presented.

This research was undertaken for the purpose of investigating the problem of the colors of magnesium, calcium and barium tetracyanoplatinates (II) in the crystalline state. In this work the dichroism of the crystals of $BaPt(CN)_4 \cdot 4H_2O$, $CaPt(CN)_4 \cdot 5H_2O$ and $MgPt(CN)_4 \cdot 7H_2O$ was measured, and this phenomenon is discussed in relation to the crystal structure.

## Experimental

**Measurement.**—Quantitative dichroism measurements of the crystals were carried out by the microscopic method with microcrystals, as described in the previous report[1]. $\alpha$ denotes absorption coefficient per mm. of the crystal, and //- or $\perp$-absorption represents that of polarized light with electric vector parallel or perpendicular, respectively, to the complex plane.

Extinction coefficients, $\varepsilon$, of barium tetracyanoplatinate (II) in aqueous solution were determined by the photographic method using a sector photometer[2]. Aqueous solutions of the complex salt were $3.3\times10^{-3}$, $1.3\times10^{-4}$ and $3.3\times10^{-5}$ molar. Measurements were made at room temperature.

**Materials.—$BaPt(CN)_4 \cdot 4H_2O$.** The pure yellow compound was obtained as monoclinic prisms by recrystallizing a sample of the compound of commercial reagent grade. The crystal structure has been studied by Brasseur and de Rassenfosse[3].

**$CaPt(CN)_4 \cdot 5H_2O$.** It was prepared from aqueous solutions of barium tetracyanoplatinate (II) and calcium sulfate as yellow, orthorhombic, prismatic crystals. The crystal structure has not been completely analyzed, although the lattice constants and the unit cell have been determined[4].

**$MgPt(CN)_4 \cdot 7H_2O$.** It was prepared from aqueous solutions of the barium salt and magnesium sulfate. Red, tetragonal, prismatic crystals with green metallic luster were obtained. The crystal structure has been studied by Pauling and Bozorth[5].

## Results and Discussion

**The Crystal Structure of $CaPt(CN)_4 \cdot 5H_2O$.**—The crystal structure of the calcium salt has not been determined as yet. Absorption spectrum of this crystal by polarized light perpendicular to the $c$-axis, however, bears a striking resemblance to //-absorptions of both barium and magnesium salts, each of them showing a sharp, characteristic absorption band

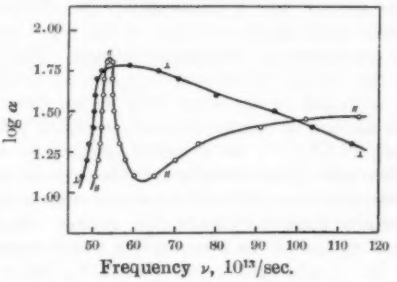


Fig. 1.—Dichroism of $MgPt(CN)_4 \cdot 7H_2O$.

(1) S. Yamada, *J. Am. Chem. Soc.* **73**, 1182 (1951)

(2) The study of J. A. Khvostikov (*Physik. Z. Sowjetunion*, **9**, 211 (1936)) states that aqueous solutions of magnesium, barium and potassium salts show the same absorption spectra.

(3) H. Brasseur and A. de Rassenfosse, *Z. Krist.*, **88**, 210, 221 (1934).

(4) H. Brasseur and A. de Rassenfosse, *Bull. soc. roy. sci. Liège*, **4**, 24 (1935).

(5) R. M. Bozorth and L. Pauling, *Phys. Rev.*, **39**, 538 (1932).

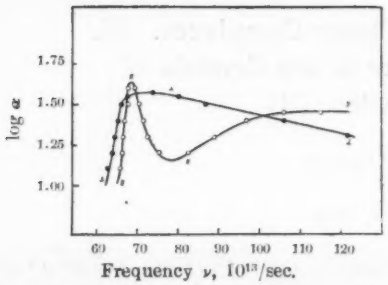


Fig. 2.—Dichroism of $CaPt(CN)_4 \cdot 5H_2O$.

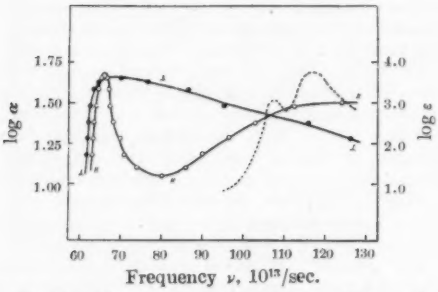


Fig. 3.—Dichroism of $BaPt(CN)_4 \cdot 4H_2O$ and absorption spectrum of aqueous solution (dotted curve).

of the same kind, which has scarcely ever been found in the crystals previously measured. On the other hand, the absorption spectrum of the calcium salt by polarized light parallel to the *c*-axis is similar to ⊥-absorption of the other salts. Now, according to the hypotheses that absorption by the calcium salt of polarized light perpendicular to the *c*-axis corresponds to //-absorption and that the other absorption corresponds to ⊥-absorption, its dichroism seems quite similar to that of the other salts. In consequence, tetracyanoplatinate (II) ions in the crystal of calcium salt are assumed to be arranged in the same way as in those of the barium or magnesium salt, in which planar ions, $Pt(CN)_4^{--}$, are oriented parallel to each other and perpendicular to the *c*-axis, with platinum ions disposed in equal distances on straight lines parallel to the *c*-axis. On the basis of the above presumption was designated //-or ⊥-absorption for $CaPt(CN)_4 \cdot 5H_2O$ in Fig. 2.

**The State of the Complex Ions in Crystals.**—First, the fact that the crystals of these three compounds show similar dichroism, different from each other only in the position of the absorption band, suggests that the complex ions undergo quite similar effects in these three compounds[6]. Secondly, it is recognized from the figures that ⊥-absorption is both more bathochromic and more hyperchromic than //-absorption in all of these compounds, showing that the complex ion in the crystalline state is influenced more effectively in the direction perpendicular to the complex plane than in the plane, and that the force is exerted perpendicularly upon it. Thirdly, the order of bathochromicity for the sharp bands of the //-absorptions (Table 1) indicates that the effect

Table 1

Characteristic Bands of //-Absorption

| | Shortest dist. between Pt ions | Frequency at abs. max. $sec^{-1}$ | Half width, $sec^{-1}$. |
|---|---|---|---|
| $MgPt(CN)_4 \cdot 7H_2O$ | 3.13[a] Å. | $54.0 \times 10^{13}$ | $2.8 \times 10^{13}$ |
| $CaPt(CN)_4 \cdot 5H_2O$ | 3.32[b] Å. | 68.6 | 5.4 |
| $BaPt(CN)_4 \cdot 4H_2O$ | 3.27[c] Å. | 65.8 | 4.6 |
| $[Pt(NH_3)_4][PtCl_4]$ | 3.21[d] Å. | | |

(a) Ref. 5.
(b) This value was estimated on the basis of the crystal structure assumed in this report and from the data given in Ref. 3.
(c) Ref. 4.
(d) E. G. Cox, F. W. Pinkard, W. Wardlaw and G. H. Preston, *J. Chem. Soc.*, **1932**, 2527.

upon the complex ion increases in the order Ca, Ba and Mg salts, since the larger the effect on the complex ion, the more bathochromically the absorption would be displaced. This order is in conformity with the increasing order of sharpness of the characteristic band (Table 1), but differs from the order of strength of the cations expected from the periodic table.

From the foregoing considerations, it is concluded that the force on the complex ions in the crystal differs from the Coulombic force between the cation and the complex anion. As to the force in these crystals, direct interaction between complex ions, of the same kind as was suggested for Magnus' salt in the previous report[7], is proposed. Thus, in these crystals, the mutual interaction between central platinum ions of planar complex ions is supposed to be exerted upon one another, where the pairs of electrons in coordination above and below the central platinum would contribute in a considerable degree. The considerably smaller interplatinic distance for the magnesium salt as compared with that for

(6) It is quite clear from comparison of the absorption spectra of the crystals and of the solution that complex ions in the crystals are in a condition quite different from their state in solution.
(7) S. Yamada, *J. Am. Chem. Soc.*, **73**, 1579 (1951)

Magnus' salt would allow us to expect larger interaction between complex ions in the former than in the latter. The distances in cases of both barium and calcium salts are considered to be short enough for direct interaction to be expected between complex ions.

Thus, it is concluded that, as the distance between platinum ions becomes smaller and, in consequence, the interaction stronger in the order of Ca, Ba and Mg salts (Table 1), the absorption is displaced toward longer wave-length and the characteristic band of //-absorption becomes sharper. It may be supposed that, as the interaction between platinum ions increases in the order Ca, Ba and Mg salts, the prismatic aggregates of $Pt(CN)_4^{--}$ ions are more firmly connected together through platinum ions, with the result that a new electronic system is formed and the absorption suffers bathochromic effects, the characteristic band of //-absorption increasing in sharpness. The interaction between platinum ions in these tetracyanoplatinates (II) is extraordinary as compared to that in Magnus' salt; in the latter the interaction is reinforced by Coulombic attraction between complex ions of opposite electrical charges, while in the former there must be instead a repulsion between complex anions of the same sign.

**Summary**

The dichroism of crystals of $BaPt(CN)_4 \cdot 4H_2O$, $CaPt(CN)_4 \cdot 5H_2O$ and $MgPt(CN)_4 \cdot 7H_2O$ has been measured in the visible and the near-ultraviolet region, and with the aid of results of this measurement, the state of the complex ions in the crystals has been discussed in relation to their crystal structures. These crystals show similar dichroism, with the characteristic sharp absorption band for //-absorption. It has been concluded that between adjacent tetragonal complex ions piled upon one another along the *c*-axis in these crystals there exists a sort of direct interaction, which is supposed to be related to the unusual colors of these compounds. It has been found that as the distance between platinums decreases in the order of Ca, Ba and Mg salts, the interaction between platinum ions becomes stronger, and that the characteristic band becomes sharper and is displaced towards longer wave-length. The interaction in these crystals is regarded as more remarkable than that in Magnus' salt.

The author wishes to express his sincerest thanks to Professor R. Tsuchida for his advices and encouragement throughout the work.

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# Fundamental Studies on the Current-Voltage Curve in Polarography. IV. On the Reduction Wave of Organic Compounds——Especially on the Wave which Involves the "Kinetic Current"

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There exist many possible types of the redox reaction of organic compounds at the dropping mercury electrode surface, and the formulae of the polarographic current-voltage curve will take various forms according to the type of the reaction. In the present paper, the case in which the undissociated molecule of an organic acid is reduced at the more positive potential than the corresponding dissociated anion has been investigated. After deriving the general formulae for the current-voltage curve, the special case which involves the "kinetic current" has been considered, and the discussions on some properties of the polarographic waves of pyruvic acid[1] have been carried out.

## Derivation of the General Formulae

Let us consider that in the body of the solution the equilibrium between the dissociated

(1) R. Brdička, *Collection Czechoslov. Chem. Communs.*, **12**, 212 (1947).

anion, A′, and the undissociated molecule, HA, is kept according to the following equation:

$$A' + H^+ \underset{k_4}{\overset{k_3}{\rightleftharpoons}} HA \qquad (1)$$

On the other hand, at the electrode surface the undissociated molecule combines with the electrons and then the reduced ion, $R^-$, reacts with the hydrogen ions getting the reduced molecule, $RH_2$.

$$HA + 2\varepsilon \underset{\kappa_2 E_2}{\overset{\kappa_1 E_1}{\rightleftharpoons}} R^- \qquad (2)$$

$$R^- + 2H^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} RH_2 \qquad (3)$$

It is assumed that the equilibrium concentration of the undissociated molecule at the electrode surface is maintained by the diffusion process from the interior of the solution and by the recombination reaction at the electrode surface (the forward reaction of process (1)). Furthermore, accompanying these processes at the electrode surface, the diffusion process of the hydrogen ion between the body of the solution and the electrode surface comes into cosideration. Under these conditions the current flowing at the electrode surface can be represented by the following equations:

$$\begin{aligned} I &= 2\varepsilon K_{HA}([C_{HA}]^\circ - [C_{HA}]) \\ &\quad + 2\varepsilon K_{A'}([C_{A'}]^\circ - [C_{A'}]) \\ &= 2\varepsilon K_{HA}'([A_{HA}]^\circ - [A_{HA}]) \\ &\quad + 2\varepsilon K_{A'}'([A_{A'}]^\circ - [A_{A'}]) \\ &= I_{HA} + I_k^{(2)} \end{aligned} \qquad (4)$$

$$I = 2\varepsilon(\kappa_1 E_1 [A_{HA}] - \kappa_2 E_2 [A_{R^-}]) \qquad (5)$$

$$\begin{aligned} I_k &= 2\varepsilon\sigma(k_3[A_{H^+}][A_{A'}] - k_4[A_{HA}]) \\ &= 2\varepsilon(k_3'[A_{A'}] - k_4'[A_{HA}]), \\ k_3' &\equiv \sigma k_3[A_{H^+}],\ k_4' \equiv \sigma k_4 \end{aligned} \qquad (6)$$

$$\begin{aligned} I &= 2\varepsilon\sigma(k_1[A_{H^+}]^2[A_{R^-}] - k_2[A_{RH_2}]) \\ &= 2\varepsilon(k_1'[A_{R^-}] - k_2'[A_{RH_2}]), \\ k_1' &\equiv \sigma k_1[A_{H^+}]^2,\ k_2' \equiv \sigma k_2 \end{aligned} \qquad (7)$$

$$\begin{aligned} I &= 2\varepsilon K_{RH_2}([C_{RH_2}] - [C_{RH_2}]^\circ) \\ &= 2\varepsilon K_{RH_2}'([A_{RH_2}] - [A_{RH_2}]^\circ) \end{aligned} \qquad (8)$$

$$\begin{aligned} I &= 2\varepsilon K_{H^+}'([C_{A^+}]^\circ - [C_{A^+}]) \\ &= 2\varepsilon K_{H^+}'([A_{A^+}]^\circ - [A_{H^+}]) \end{aligned} \qquad (9)$$

$\sigma$: the constant concerning the nature of the electrode.

$[C]^\circ$, $[C]$: concentrations in the body of the solution and at the electrode surface.

$[A]^\circ$, $[A]$: activities in the body of the solution and at the electrode surface.

$K$: the constant concerning the diffusion process.

$K' \equiv K/f$, $f$ is the activity-coefficient.

$k_1' \sim k_4'$, $\kappa_1 E_1$, $\kappa_2 E_2$: the terms concerning the reaction rates of the corresponding processes.[3]

If the solution is well buffered, however, the diffusion process of the hydrogen ion can be neglected and $[A_{A'}]$ is considered to be equal to $[A_{A'}]^\circ$. In this paper such a case only has been dealt with.

Generally, the two constants, $K_{HA}$ and $K_{A'}$, concerning the diffusion coefficients of the undissociated molecule and the dissociated anion, are nearly the same, and can be written as $K$, so that Eq. (4) is reduced to

$$\begin{aligned} I &= 2\varepsilon K_O([C_O]^\circ - [C_O]) \\ &= 2\varepsilon K_O'([A_O]^\circ - [A_O]), \end{aligned} \qquad (10)$$

where $[C_O]^\circ$ and $[C_O]$ are the analytical concentrations of the oxidized form in the body of the solution and at the electrode surface, which can be represented by the relations

$$\begin{aligned} [C_O]^\circ &= [C_{HA}]^\circ + [C_{A'}]^\circ, \\ [C_O] &= [C_{HA}] + [C_{A'}]. \end{aligned}$$

$[A_O]^\circ$ and $[A_O]$ are the activities of the corresponding terms. By eliminating $[A_{RH_2}]$, $[A_{R^-}]$ and $[A_{HA}]$ from these equations the formula

$$\begin{aligned} I/2\varepsilon = \kappa_1 E_1 \frac{k_3'(K_O'[A_O]^\circ - I) - K_O' I_k}{K_O'(k_3' + k_4')} \\ - \kappa_2 E_2 \frac{k_2'(K_O'[A_O]^\circ + I) + K_O' I}{K_O' k_1'} \end{aligned}$$

is obtained. Now, let us introduce the relation

$$I_k = \rho I \qquad (11)$$

where $\rho$ is a proportional constant. Then the relation between the current and the electrode potential can be written as follows:

$$I, 2\varepsilon = \frac{[A_O]^\circ - [E][A_{RH_2}]^\circ}{\frac{1}{[\kappa_1 E_1]} + \left(\frac{1}{K_O'} + \frac{\rho}{k_3'}\right) + [E]\left(\frac{1}{K_O'} + \frac{1}{k_4'}\right)} \qquad (12)$$

(2) R. Brdička and K. Wiesner, *Collection Czechoslov. Chem. Communs.*, **12**, 138 (1947).

(3) The explanations for $\kappa_1 E_1$ and $\kappa_2 E_2$ were set down in the previous papers (N. Tanaka and R. Tamamushi, *Bull. Chem. Soc. Japan*, **22**, 187 (1949), etc.).

$$= \frac{[E]'[A_O]^\circ - [A_{RH_2}]^\circ}{\frac{1}{[\kappa_2 E_2]} + \left(\frac{1}{K_R'} + \frac{1}{k_2'}\right) + [E]'\left(\frac{1}{K_O'} + \frac{\rho}{k_3'}\right)} \quad (12')$$

where

$$[\kappa_1 E_1] \equiv \frac{k_3'}{k_3' + k_4'} \kappa_1 E_1, \quad [\kappa_2 E_2] \equiv \frac{k_2'}{k_1'} \kappa_2 E_2 \quad (13)$$

$$[E] \equiv \frac{[\kappa_2 E_2]}{[\kappa_1 E_1]}, \qquad [E]' \equiv \frac{[\kappa_1 E_1]}{[\kappa_2 E_2]}$$

Eqs. (12) and (12') are the general formulae of the oxidation-reduction wave which appears according to the electrode processes (1)-(3).

The formulae for the various conditions can be derived by the same method as mentioned in the previous papers, because general formulae (12) and (12') are quite analogous with those of the complex metal ion.[4] In the following section, the theoretical analysis of the wave will be set down under the condition that the terms $k_2'$ and $k_3'$ are comparable with $K_O'$ and $K_R'$.

## The Case When $k_2'$ and $k_3'$ are Comparable with $K_O'$ and $K_R'$

Now, two special cases can be considered according to the relative magnitudes of the terms, $k_2'$, $k_3'$, $K_O'$, $K_R'$, $[\kappa_1 E_1]$ and $[\kappa_2 E_2]$. One of them is the case when $k_2'$, $k_3'$, $K_O'$, and $K_R'$ are much smaller than $[\kappa_1 E_1]$ and $[\kappa_2 E_2]$ at the electrode potential where $[\kappa_1 E_1]$ is nearly equal to $[\kappa_2 E_2]$, and the other case is that in which the relation between these terms is reverse. The latter corresponds to the activation-controlled one, and only the discussion on the reduction wave obtained in such a case is carried out in the present paper.

If the rate-determining step of the over-all electrode process is the activation process which contains the transfer of the electrons, the condition that $1/[\kappa_1 E_1]$ is much larger than both of $1/K_O' + \rho/k_3'$ and $1/K_R' + 1/k_2'$ is satisfied at the electrode potential where $[\kappa_1 E_1]$ is nearly equal to $[\kappa_2 E_2]$. According to the value of the electrode potential the following three cases are considered, *i. e.*, $[\kappa_1 E_1] \cong [\kappa_2 E_2]$ (Part A), $[\kappa_1 E_1] \gg [\kappa_2 E_2]$ (Part B), and $[\kappa_1 E_1] \ll [\kappa_2 E_2]$ (Part C).[4),5)]

**Part A.** $[\kappa_1 E_1] \cong [\kappa_2 E_2]$

In this potential region the current flowing is represented as follows:

$$I/2\mathcal{E} = [\kappa_1 E_1][A_O]^\circ - [\kappa_2 E_2][A_{RH_2}]^\circ, \quad (14)$$

and the current is completely defined by the activation process. The equation for the potential where the current flowing is zero can be derived from the above equation.

**Part B.** $[\kappa_1 E_1] \gg [\kappa_2 E_2]$

(1) $1/[\kappa_1 E_1] \cong 1/K_O' + \rho\, k_3'$

In this case the equations for the reduction wave,

$$I/2\mathcal{E} = \frac{[A_O]^\circ}{\frac{1}{[\kappa_1 E_1]} + \left(\frac{1}{K_O'} + \frac{\rho}{k_3'}\right)} \quad (15)$$

or

$$[\kappa_1 E_1] = K_O' \frac{(I_l)_O}{(I_d)_O} \frac{I}{(I_l)_O - I}$$

are derived, where $(I_d)_O$ equals $2\mathcal{E}K_O'[A_O]^\circ$ and $(I_l)_O$ represents the limiting current of the wave. The detailed discussion of the limiting current, $(I_l)_O$, will be carried out in the following.

(2) $1/[\kappa_1 E_1] \ll 1/K_O' + \rho\, k_3'$

Now, the limiting current is obtained, and it is represented as follows:

$$(I_l)_O = \frac{1}{K_O'} \frac{(I_d)_O}{\frac{1}{K_O'} + \frac{\rho}{k_3'}} = \frac{k_3'(I_d)_O}{k_3' + \rho K_O'}$$

**Part C.** $[\kappa_1 E_1] \ll [\kappa_2 E_2]$

This is the potential region for the oxidation wave,[5] but all discussions on this part are omitted in this paper.

In the following section some discussions will be made on the properties of the reduction wave by means of the equations derived above.

**Analysis of the Limiting Current.**—It can be considered that the limiting current, $(I_l)$, is the sum of the term $(I_d)_{HA}$ due to the diffusion process of the undissociated molecule HA and the term $I_k$ which is attributed to the recombination reaction (3), *i. e.*,

$$(I_l)_O = (I_d)_{HA} + I_k. \quad (17)$$

By the definition of $\rho$, previously mentioned, the relation

$$\rho = \frac{I_k}{(I_l)_O} = \frac{(I_l)_O - (I_d)_{HA}}{(I_l)_O}$$

is derived, and if $[A_{HA}]^\circ$ is the activity of the undissociated molecule in the body of the solution the term $(I_d)_{HA}$ can be written as follows:

$$(I_d)_{HA} = 2\mathcal{E}K_O'[A_{HA}]^\circ$$

(4) R. Tamamushi and N. Tanaka, *Bull. Chem. Soc. Japan*, **23**, 110 (1950).
(5) R. Tamamushi and N. Tanaka, *ibid.*, **22**, 227 (1949).

Moreover, as it can be considered that in the body of the solution the dissociation equilibrium is maintained, $\rho$ can be represented as below by means of the relations cited above.

$$\rho = \frac{(I_l)_0 - 2\varepsilon K_0'[A_0]^\circ \dfrac{[A_H^+]}{[A_H^+]+\Gamma}}{(I_l)_0} = \frac{(I_l)_0 - (I_d)_0 \dfrac{[A_H^+]}{[A_H^+]+\Gamma}}{(I_l)_0} \tag{18}$$

$\Gamma$ means the dissociation constant of the molecule, HA, and is equal to $k_4/k_3$. When the terms $(I_d)_0$, $\Gamma$ and $[A_H^+]$ are known, the value of $\rho$ can be calculated by Eq. (18). By introducing this relation into Eq. (16) we can write $(I_l)_0$ in terms of $(I_d)_0$, $\Gamma$ and $[A_H^+]$, *i. e.*,

$$(I_l)_0 = (I_d)_0 \frac{k_3'(\Gamma+[A_H^+])+K_0'[A_H^+]}{(k_3'+K_0')([A_H^+]+\Gamma)} = 2\varepsilon \frac{K_0'[A_0]^\circ[A_H^+]}{\Gamma+[A_H^+]} \frac{\sigma k_3(\Gamma+[A_H^+])+K_0'}{K_0'+\sigma k_3[A_H^+]} \tag{19}$$

This formula is quite the same as has been set down by R. Brdička for the "kinetic current."[2] Furthermore, if we take into account the relation obtained by Brdička, the constant $\sigma$ can be written as follows:[2]

$$\sigma = q \cdot \mu \cdot 10^{-3} \text{ [6]} \tag{20}$$

$q$: the surface area of the dropping mercury electrode in cm.$^2$

$\mu$: the thickness of the reaction layer at the electrode surface in cm.

**On the Rate of the Recombination Reaction.**—The following relation for $k_3'$ is easily obtained from Eq. (16)

$$k_3' = \sigma k_3[A_H^+] = \frac{K_0'\rho(I_l)_0}{(I_d)_0-(I_l)_0} \tag{21}$$

Therefore, if $(I_d)_0$, $(I_l)_0$, $K_0'$, and $\rho$ are known from the experimental data and others, the terms $k_3'$, $\sigma k_3$, and $\mu k_3$ can be calculated from Eqs. (20) and (21). If we use the theoretical expression for $\mu$ obtained by J. Koutecky and R. Brdička[7]

$$\mu = \sqrt{\frac{D}{k_3\Gamma}}$$

the equation for $k_3$,

$$k_3 = \frac{(\mu k_3)^2\Gamma}{D} \text{ sec.}^{-1}(\text{mol/liter})^{-1}, \tag{22}$$

is obtained, where $D$ is the diffusion constant of the depolarizer. Hence the value of $k_3$ can be determined from the experiments.

Moreover, by means of the ratio, $(I_l)_0/(I_d)_0 = T$, the equation

$$k_3' = \frac{K_0'[T\Gamma-[A_H^+](1-T)]}{(\Gamma+[A_H^+])(1-T)} \tag{23}$$

is derived.

**The Relation between $V$ and $\log I/((I_l)_0-I)$.**—This relation is a straight line whose tangent is $0.059/2\alpha$ volt at 25°, if the value of $\alpha$ is constant. From this tangent the value of $\alpha$ can be calculated.

**Half-wave Potential.**—By introducing the relation, $I = (I_l)_0/2$, for the current at the half-wave potential, the equation

$$[\kappa_1 E_1]_{1/2} = \frac{k_3'K_0'}{k_3'+\rho K_0'} \tag{24}$$

is obtained from Eq. (15), and, furthermore, this formula can be written as follows by means of relation (13) and the definition of $\Gamma$,

$$V_{1/2} = \frac{RT}{2\alpha F}\left(\ln s\frac{kT}{h} - \ln K_0'\right) - \frac{RT}{2\alpha F}\ln\frac{\sigma k_3([A_H^+]+\Gamma)}{\sigma k_3[A_H^+]+\rho K_0'} - \frac{\Delta F_1}{2\alpha F} = \text{const.} - \frac{RT}{2\alpha F}\ln\frac{\sigma k_3([A_H^+]+\Gamma)}{\sigma k_3[A_H^+]+\rho K_0'} \tag{24'}$$

$s$: the constant concerning the nature of the electrode.

It can be said that $V_{1/2}$ is constant and independent of the activity of the substance concerned, if $p$H, $\alpha$ and the ionic strength of the solution remain constant. If the values of $K_0'$, $k_3'$, $\Gamma$, $\rho$, $\alpha$, and others are known, the free energy of the activation, $\Delta F_1$, can be calculated from the formula mentioned above.

Now, let us consider the relation between $V_{1/2}$ and $p$H. Representing the half-wave potentials corresponding to the hydrogen ion concentrations $[A_H^+]_a$ and $[A_H^+]_b$ by $(V_{1/2})_a$ and $(V_{1/2})_b$, respectively, then for the shift of the half-wave potential with respect to the change of $p$H the following relation is obtained:

$$(V_{1/2})_a-(V_{1/2})_b = \Delta V_{1/2} = \frac{RT}{2\alpha F}\ln\frac{([A_H^+]_b+\Gamma)(\sigma k_3[A_H^+]_a+K_0'\rho_a)}{([A_H^+]_a+\Gamma)(\sigma k_3[A_H^+]_b+K_0'\rho_b)} \tag{25}$$

(6) In this case the unit of the concentration is mol per liter.

(7) J. Koutecky and R. Brdička, *Collection Czechoslov. Chem. Communs.*, **12**, 337 (1947).

It is found from Eqs. (24′) and (25) that when the value of $p$H is large the value of $V_{1/2}$ becomes independent of $p$H and reaches a constant value, and this can be thought as a special character of the reduction wave which is obtained under the condition mentioned above (Fig. 1).

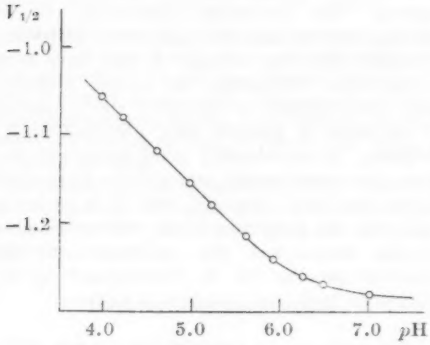


Fig. 1.

Hitherto, the case, in which $K_a'$, $K_K'$, $k_2'$ and $k_3'$ have the values nearly of the same order, has been discussed. The important character in such a case is that the limiting current is not represented only by the rate of the diffusion process but also by the term concerning the reaction rate such as $k_3'$. For such a limiting current, it is obvious that the application of the Ilkovič' equation fails, and the "kinetic current" mentioned by Brdička corresponds to this current. We can distinguish the "kinetic current" from the ordinary "diffusion current" by its dependence on the nature of the electrode, temperature and so forth.[1],[2]

As for the example of the application of the theoretical results obtained above, the shift of the half-wave potential and the calculation of the free enery of the activation, $\Delta F_1$, of the reduction process of pyruvic acid are discussed in the following section.

## Discussion on the Properties of the Reduction Wave of Pyruvic Acid[1]

The polarographic study on the pyruvic and phenylglyoxylic acids was carried out, at first, by O. H. Müller,[8] and recently by R. Brdička.[1] The latter has explained the appearance of the double-wave by introducing the conception of the "kinetic current." However, the shift of the half-wave potential accompanying the change of $p$H has not yet been interpreted.

(8) O. H. Müller, *J. Am. Chem. Soc.*, **61**, 390 (1939).

By means of the theoretical equations described above, the discussion on the half-wave potential and the calculation of the value of $\Delta F_1$ can be carried out. The experimental data obtained by Brdička have been used for the present calculation.

**Calculation of the Shift of the Half-wave Potential.**—First, the linear relations have been found between $V$ and $\log I/(I_l-I)$ for the actual polarograms of pyruvic and phenylglyoxylic acids. From these relations the value of $\alpha$ for each case has been calculated. While the value of $\alpha$ for pyruvic acid has been nearly constant and equal to 0.28, on the other hand, that of phenylglyoxylic acid varied from 0.54 to 0.34 according to the change of $p$H. Unless the value of $\alpha$ remains constant, it is quite doubtful whether Eqs. (24′) and (25) can be applicable or not for the present purpose, so only the calculation for pyruvic acid will be carried out in the following.

After having been determined the value of $\alpha$, the term $\mu k_3$ has been calculated from Eqs. (20) and (21), the mean value of which over the range of $p$H 4.95-6.81 is $3.2\times10^5$. The terms $\rho$, $K_a'$ and $m^{2/3}t^{1/6}$ (the capillary constant) have been obtained from the polarograms observed by Brdička, and for the value of $\Gamma$, $4\times10^{-3}$ has been used. Then, the shift of the half-wave potential with the change of $p$H has been calculated from Eq. (25), and the results have been compared with the experimental data obtained by Brdička (Table 1). The half-wave potential of the wave at $p$H=5.20 (−1.180 volts)

Table 1

| $p$H | $\Delta V_{1/2}$ *calc.*, mV. | $\Delta V_{1/2}$ *obs.*, mV. | $p$H | $\Delta V_{1/2}$ *calc.*, mV. | $\Delta V_{1/2}$ *obs.*, mV. |
|---|---|---|---|---|---|
| 3.95 | 127 | 114 | 5.59 | −35 | −35 |
| 4.19 | 102 | 90 | 5.91 | −60 | −60 |
| 4.58 | 61 | 65 | 6.24 | −79 | −80 |
| 4.95 | 24 | 28 | 6.48 | −89 | −80 |
| 5.20 | — | — | 6.64 | −93 | — |

has been taken as the standard for the present calculation. It has been shown by the experimental results that half-wave potential of such a wave tends to reach the constant value when $p$H increases. This property can be completely interpreted by Eq. (25), and the calculated limiting value of the half-wave potential for pyruvic acid is obtained to be −1.287 volts. From this result it can be said that the theoretical treatement mentioned above can interpret the properties of the wave of pyruvic acid at least qualitatively.

**Calculation of $\Delta F_1$.**—Introducing the values

of $\alpha$, $\sigma k_3$, $\rho$, and others to Eq. (24′) the value of the free energy of the activation for the forward reaction of the process (2), $\Delta F_1$, can be calculated.[9] In the case of pyruvic acid the results obtained over the range of $p$H 4.95-6.48 are shown in Table 2.

Table 2

| $p$H | $V_{1/2}$, volt | $\Delta F_1$, joule |
|---|---|---|
| 4.95 | −1.152 | $9.5\times10^{4}$ |
| 5.20 | −1.180 | $9.5\times10^{4}$ |
| 5.59 | −1.215 | $9.6\times10^{4}$ |
| 5.91 | −1.240 | $9.6\times10^{4}$ |
| 6.24 | −1.260 | $9.6\times10^{4}$ |
| 6.49 | −1.260 | $9.5\times10^{4}$ |
| | mean value..... | $9.6\times10^{4}$ |

## Summary

Of the oxidation-reduction reaction of organic compounds, the case, in which the undissociated molecule of an organic acid is reduced at the more positive potential than the corresponding dissociated anion and the equilibrium concentration of the reducible form at the electrode surface is kept by the diffusion process and the recombination reaction at the electrode surface, has been taken into consideration. Under such conditions, the general formulae for the polarographic current-voltage curve have been derived, and the special case which involves the "kinetic current" has been investigated. The theoretical discussions on the limiting current and the shift of the half-wave potential with the change of $p$H have been carried out. Moreover, the results obtained have been applied to interpret the properties of the wave of pyruvic acid observed by R. Brdička. A considerably good agreement between the experimental data and the theoretical results has been obtained, and it is probably said that the properties of the various polarographic waves and the mechanism of the electrode process can be investigated by the analogous treatment mentioned above.

The authors are grateful to express their thanks to the Ministry of Education for its financial support.

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(9) The constant $s$ in Eq. (24′) is assumed to be equal to the constant $\sigma$.

# Effect of Gelatin on the Polarographic Waves of *p*- and *o*-Nitroanilines

By Nobuyuki TANAKA and Masako KOBAYASHI

(Received March 12, 1951)

Several literatures have been published on the studies on polarographic reduction waves of nitroanilines. In 1932, M. Shikata and E. Taguchi[1] reported on the reduction potentials of *o*-, *m*- and *p*-nitroanilines measured by the 45° tangent method in a wide range of $p$H with buffered and non-buffered solutions, and they discussed the relation between the reduction potentials and the constitutions. Recently O. D. Shreve and E. C. Markham[2] reported on the effect of ethyl alcohol on the polarographic waves of nitroanilines. Y. Yasumori[3] tried to apply the polarographic waves of *p*- and *o*-nitroanilines to the simultaneous determination of these compounds in their mixtures, when he employed the double waves of these compounds which were obtained in supporting electrolyte of a suitable $p$H and a suitable concentration of ethyl alcohol. However, these researchers told of nothing concerning the effect of gelatin on the reduction waves of these compounds.

In the present paper are reported the effect of gelatin on the polarographic waves of *p*- and *o*-nitroanilines and its application to the determination of these compounds. The experiments and discussions on the characteristics of the polarographic waves themselves of these compounds and the reduction mechanisms will be reported elsewhere.

(1) M. Shikata and E. Taguchi, *J. Agricul. Soc. Japan*, **8**, 1225 (1932).

(2) O. D. Shreve and E. C. Markham, *J. Am. Chem. Soc.*, **71**, 2993 (1949).

(3) private communication.

## Experimental

**Apparatus.**—A Heyrovsky-Shikata type polarograph was employed. A dropping mercury electrode was employed for the cathode, and a normal calomel electrode, for the anode. The capillary constant, $m^{2/3}\ t^{1/6}$, was 1.124 ($mg.^{2/3}\ sec.^{-1/2}$), measured in distilled water free from oxygen without applied potential. All measurements were carried out in a thermostat of 25° or 30°.

**Reagents.**—*p*- and *o*-Nitroanilines were kindly given by Nippon Kasei Chemical Industries Limited, which have the melting points of 148.0-148.5° and 72.0-72.5° respectively. Their standard solutions were prepared by dissolving them in distilled water, the concentrations of which were about 1 millimol per liter.

The Clark and Lub's buffer of *p*H 9.0 was used as a supporting electrolyte solution, its actual *p*H value being 8.8 determined with an antimony electrode.

## Results and Discussion

The polarographic waves of *p*- and *o*-nitroanilines measured in the supporting electrolyte containing no gelatin are shown in Fig. 1, on which distinct maxima appeared. These maxima were suppressed by adding 0.005-0.01% of gelatin to the supporting electrolyte. When

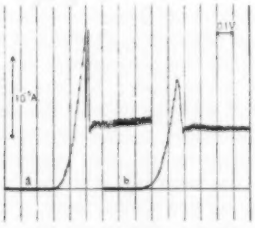


Fig. 1.—Polarograms of *p*- and *o*-nitroanilines in the supporting electrolyte containing no gelatin; (a) *p*-nitroaniline ($0.5\times10^{-5}\ M$), (b) *o*-nitroaniline ($0.5\times10^{-5}\ M$). Each poralogram beings at −0.4 volt *vs.* N. C. E.

the concentration of gelatin increased more than about 0.01%, it was found that the wave of nitroaniline splitted into two waves. The total height of the double wave was almost constant independently of the concentration of gelatin. The ratio of the wave height of the second wave to the first one became greater with the increase of the concentration of gelatin contained in supporting electrolyte. These phenomena are shown in Figs. 2 and 3.

In addition to the fact it became clear that the ratio of the second wave to the first one was different between *p*- and *o*-compounds when the supporting electrolyte contained the

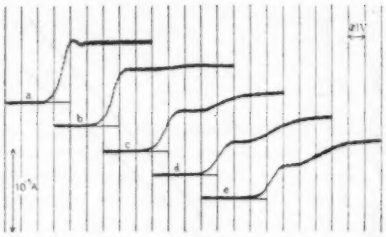


Fig. 2.—Polarograms of *p*-nitroaniline ($0.5\times10^{-5}\ M$) in the supporting electrolytes containing gelatin of, (a) 0.005%, (b) 0.01%, (c) 0.02%, (d) 0.05% and (e) 0.1%. Each polarogram begins at −0.4 volt *vs.* N. C. E.

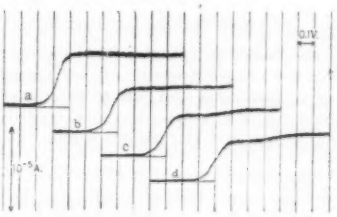


Fig. 3.—Polarograms of *o*-nitroaniline ($0.5\times10^{-5}\ M$) in the supporting electrolytes containing gelatin of, (a) 0.005%, (b) 0.01%, (c) 0.02% and (d) 0.1%. Each polarogram begins at −0.4 volt *vs.* N. C. E.

same concentration of gelatin.

The linear relations were held between the concentrations and the wave heights of both the first and the second waves of each compound, as shown in Figs. 4 and 5. Therefore,

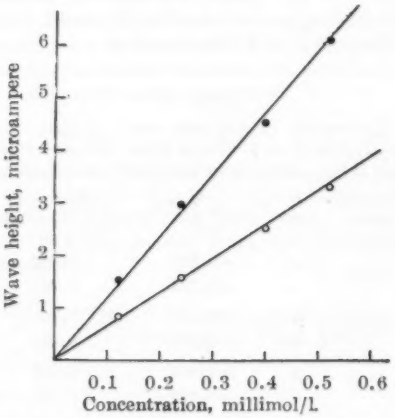


Fig. 4.—Relation between the wave height and the concentration of *p*-nitroaniline: —○—, indicates the wave height of the first wave; and —●—, the total wave height of the first and the second waves.

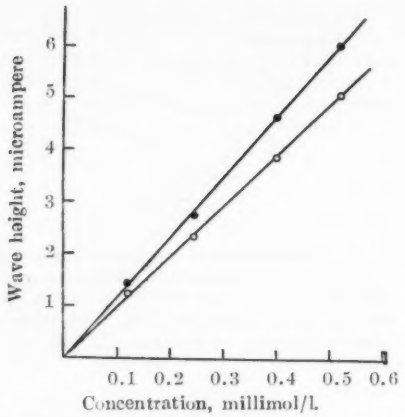


Fig. 5.—Relation between the wave height and the concentration of *o*-nitroaniline: —○—, indicates the wave height of the first wave; and —●—, the total wave height of the first and the second waves.

these double waves seemed possible to be applied to the simultaneous determination of both compounds, which will be described later.

The relations of $\log I/I_d-I$ *vs.* $V$ held straight lines, but their slopes were far less than those expected from the reversible reduction. They should hold straight lines with slopes of about 10 millivolts, if the reduction proceeded reversibly and if the numbers of electrons necessary to the reduction were six as reported by Shreve and Markham and as confirmed by the authors.

The half-wave potentials were almost independent of the concentration of the reducible substances, but shifted to negative potential with increasing concentration of gelatin, which are indicated in Tables 1 and 2.

Table 1

Half-wave Potentials and Slopes of $\log I/(I_d-I)$ *vs.* $V$ of the First Waves of *p*- and *o*-Nitroanilines in Various Concentrations

| Concentration, millimol/l. | *p* or *o* | $V_{1/2}$ *vs.* N.C.E., volt | Slope of $\log I/(I_d-I)$ *vs.* $V$, volt |
|---|---|---|---|
| 0.12 | *p* | −0.820 | 0.062 |
| | *o* | −0.791 | 0.066 |
| 0.24 | *p* | −0.814 | 0.061 |
| | *o* | −0.785 | 0.068 |
| 0.40 | *p* | −0.821 | 0.062 |
| | *o* | −0.789 | 0.068 |
| 0.52 | *p* | −0.828 | 0.071 |
| | *o* | −0.797 | 0.073 |

Supporting electrolytes contained 0.1% of gelatin.

Table 2

Half-wave Potentials and Slopes of $\log I/(I_d-I)$ *vs.* $V$ of the First Waves with the Change in the Concentration of Gelatin

| Concentration of gelatin, % | *p* or *o* | $V_{1/2}$ *vs.* N.C.E., volt | Slope of $\log I/(I_d-I)$ *vs.* $V$, volt |
|---|---|---|---|
| 0.005 | *p* | (−0.74) | — |
| | *o* | (−0.73) | — |
| 0.01 | *p* | −0.750 | 0.057 |
| | *o* | −0.756 | 0.069 |
| 0.02 | *p* | −0.772 | 0.064 |
| | *o* | −0.780 | 0.076 |
| 0.05 | *p* | −0.795 | 0.068 |
| | *o* | −0.787 | 0.075 |
| 0.1 | *p* | −0.815 | 0.069 |
| | *o* | −0.801 | 0.078 |

Concentration of *p*- and *o*-nitroanilines are 0.5 millimol per liter.

The numbers of electrons necessary to the reduction were calculated from the polarogram by means of the Ilkovič equation and the diffusion constant. For the latter, $8.79\times10^{-6}$ $cm.^2sec.^{-1}$, the value given by Shreve and Markham, was employed. The result showed that the reduction of *p*- and *o*-nitroanilines, including the second wave if the wave splitted into two waves, was of the six-electron reduction, as the same as reported by Shreve and Markham.

It seems important to answer the problems of why the wave splits by the addition of gelatin and of why the ratio of the wave height of the second wave to the first one increases with the increase of the concentration of gelatin. It has been reported that nitro compound often gives a double wave in the certain condition. Being the case, the first wave corresponds to the reduction of nitro compound to hydroxylamine, (that is, a four-electron reduction), while the second wave corresponds to the reduction of hydroxylamine (that is, a two-electron reduction).

The present case, no doubt, did not correspond to such a case, because the ratio of both waves changed continuously with increasing concentration of gelatin. The authors would like to infer that some changes at the electrode interface occurring by the addition of gelatin caused the wave splitting. Such a case has been recently reported by E. L. Colichman[4] in regard to the reduction waves of the several inorganic compounds, which are greatly influenced by surface active substances, such as gelatin and cetyltrimethylammonium bromide.

(4) E. L. Colichman, *J. Am. Chem. Soc.*, **72**, 4036 (1950).

In the present study, however, the authors could not confirm the idea, but as the result of some experiments, they did not prove the phenomenon to be explained by the idea of the formation of intermediate reduction substances and also by that of kinetic current.

## Analytical Application

Since it was found out that the wave heights are proportional to the concentration and that the ratio of wave height of the second wave to the first one is different between *p*- and *o*-compounds in the supporting electrolyte containing the same concentration of gelatin, the double waves were applied to the simultaneous determination of these compound. The concentration of gelatin contained in the supporting electrolyte was decided to be 0.1%, considering that, in the case, the difference of the ratio of the second wave to the first one was the greatest between *p*- and *o*-compounds. The relations of the wave heights and the concentrations were obtained in this condition, as shown in Figs. 4 and 5. From the result the following equations were obtained to express the concentration of each of these compounds contained in the solution electrolyzed.

Table 3

Simultaneous Determination of Synthetic Samples

| Ratio of *p*:*o* in synthetic samples, (*p* : *o*) | | Concentration present, millimol/l. | Concentration found, millimol/l. |
|---|---|---|---|
| 1 : 1 | *p* | 0.24 | 0.27 |
| | *o* | 0.24 | 0.18 |
| 2 : 1 | *p* | 0.32 | 0.35 |
| | *o* | 0.16 | 0.18 |
| 4 : 1 | *p* | 0.32 | 0.32 |
| | *o* | 0.08 | 0.06 |
| 5 : 1 | *p* | 0.40 | 0.46 |
| | *o* | 0.08 | 0.09 |
| 1 : 2 | *p* | 0.16 | 0.17 |
| | *o* | 0.32 | 0.27 |
| 1 : 3 | *p* | 0.08 | 0.08 |
| | *o* | 0.24 | 0.23 |
| 1 : 5 | *p* | 0.08 | 0.10 |
| | *o* | 0.40 | 0.39 |

$$C_p = \frac{7.9\,h_2 - 11.6\,h_1}{38.3} \quad \text{(millimol/l.)}$$

$$C_o = \frac{11.6\,h_1 - 6.4\,h_2}{38.3} \quad (\quad ,, \quad),$$

where $C_p$ and $C_o$ represent the concentrations of *p*- and *o*-nitroanilines and $h_1$ and $h_2$, the first wave height and the total wave hight both measured in microampere.

Some synthetic samples were analyzed with the procedure with the results shown in Table 3. The results were not so good, but it was concluded that an approximate content of each compound can be estimated with the procedure.

## Summary

The effect of gelatin on the polarographic waves of *p*- and *o*-nitroanilines has been investigated,

(1) Maxima of the polarographic waves of these compounds which occur in the supporting electrolyte without gelatin were supressed by adding 0.005-0.01% of gelatin to the supporting electrolyte.

(2) The wave of each of these compounds splitted into two waves when the supporting electrolyte contained more than 0.01% of gelatin.

(3) The ratio of the wave heights of the second wave to the first increased with increasing concentration of gelatin, and it was different between *p*- and *o*-compounds in the supporting electrolyte containing the same concentration of gelatin.

(4) The wave heights of the first and the second waves of each compound were proportional to the concentration.

(5) These double waves were applied to the simultaneous determination of both compounds, with the result that the procedure was available for rough estimation of content.

The authors are grateful to Nippon Kasei Chemical Industries Limited that gave them purified samples of *p*- and *o*-nitroanilines. The cost of this study has been partly defrayed from the Grant in Aid from the Ministry of Eduaction.

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# Études spectrochimiques du cyclooctatétraène ($C_8H_8$) et du $C_{10}H_{10}$

par Seinosuké MIYAKAWA, Ikuzo TANAKA et Taku UÉMURA

(Reçu le 20 mars, 1951)

## Introduction

Les propriétés du cyclooctatétraène (C.O.T.), dont la structure est théorétiquement intéressante, ont déjà été étudiées par plusieurs chimistes et physiciens.(1) Nous avons récemment publié un mémoire dans ce bulletin sur les études de la réaction photochimique et de la structure électronique de la même substance.(2) Nous avons mesuré maintenant l'absorption visible et ultraviolette du C. O. T. et du composé $C_{10}H_{10}$ en solution et à l'état gazeux. Nous avons étudié les influences sur le spectre d'absorption du C. O. T. dans sa solution de heptane normal et celle de tétrachlorure de carbone lorsqu'on y ajoute l'iode. Ces influences d'iode sur le C. O. T. peut être comparées à celles sur le benzène.

## Procédé expérimental et spectres d'absorption

Le C.O.T. et le $C_{10}H_{10}$ qui sont employés dans nos expériences sont préparés par Prof. S. Murahashi et Dr. N. Hagiwara à l'Institut de Recherche scientifique et industrielle de l'Université d'Osaka. Les échantillons sont purifiés par les distillations fractionnaires exécutées quatre fois *in vacuo* par lesquelles les parties plus volatiles et plus lourdes sont exclues. L'alcool méthylique, l'alcool éthylique, le cyclohexane, l'heptane normal et le tétrachlorure de carbone sont utilisés comme dissolvants, et purifiés par des procédés ordinaires. Nous nous sommes servis du spectrographe en quartz "QF-60" construit par Shimazu, de celui construit par Jobin et Yvon et du spectrophotomètre Spekker de Shimazu en employant 1 cm. d'épaisseur de solution pour la détermination du spectre d'absorption. Pour mesurer l'absorption de l'échantillon gazeux du C.O.T., nous avons pris, comme auparavant, l'appareil indiqué dans la figure 1.

Les conditions expérimentales que nous avons adoptées sont les suivantes, savoir: les tubes d'absorption ajoutés à deux côtés les plaques en quartz sont changés sa longueur à 4.95, 6.7 et 20.0 cm. en variant la grandeur d'extinction. Nous avons utilisé comme source lumineuse un tube à décharges d'hydrogène et nous avons employé des plaques photographiques "Fuji" (marque japonaise) et celles pour rayons cosmiques préparées spécialement au laboratoire de la compagnie Fuji-Film pour la région à 230-195 mμ au lieu d'employer celles de Schuman.

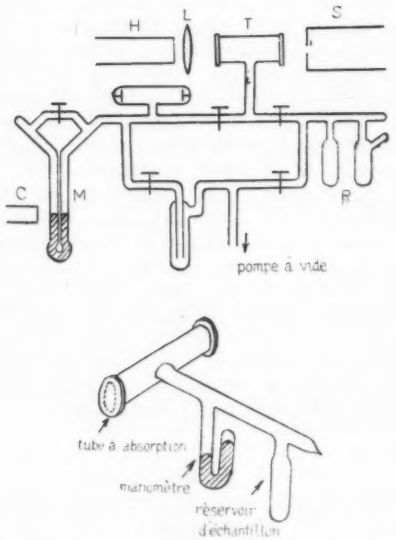


Fig. 1.—H, tube a décharges d'hydrogène; L, lentil en quartz; T, tube à absorption; S, spectrographe; C, cathétomètre; M, manomètre; R, réservoir d'échantillon.

Pour mesurer le coefficient d'absorption, on prend sept spectres sur une plaque photographique à la même durée d'exposition constante, toujours égale à 10 minutes. Six d'entre eux sont obtenus en traverssant le rayon au tube à l'absorption évacué d'avance, et ont des intensités logarithmiquement variées qui sont entre elles comme 10, 6.31, 3.98, 2.51, 1.59, 1, par le diaphragme employé pour le spectrophotomètre. Le septième obtenu par l'échantillon gazeux introduit, dans le tube à absorption sous une tension moyenne entre 3 et 6 mm. Hg et cette tension est lue sur le manomètre en mercure à l'aide du cathétomètre.

Il suffit normalement de microphotomètrer

(1) Voir les bibliographies indiquées dans ce bulletin **24**, 119(1951).

(2) Ikuzo Tanaka et Shoji Shida, ce bulletin, **23**, 54 (1950); Yuji Mori, Ikuzo Tanaka et Shoji Shida, *ibid.*, **23**, 168 (1950); Ikuzo Tanaka, Seinosuké Miyakawa et Shoji Shida, *ibid.*, **24**, 119(1951).

ces spectres, pour obtenir une courbe de noircissement de la plaque à l'aide de ces six premièrs spectres; le septième donne l'extinction gazeuse par la méthode d'interpolation. La figure 2 donne la courbe d'absorption du C. O. T. à l'état gazeux.

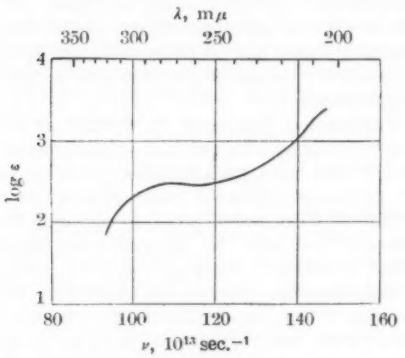


Fig. 2.—Spectre d'absorption du C. O. T. à l'état gazeux.

Dans cette figure nous avons pris le coefficient d'absorption comme celui moléculaire $\mathcal{E}$ du C. O. T. à l'état gazeux pour faire facilement comparer au cas de solution. La valeur $\mathcal{E}$ est égale à $\log I_0/I \cdot cd$, où $\log I_0/I$ est l'extinction gazeuse déjà indiquée, $d$ la longueur d'épaisseur et $c$ la concentration représenté par mol/l. Nous avons utilisé une cuve spéciale pour mesurer l'absorption entre 230 mμ et 200 mμ. Cette cuve consiste de trois parties, savoir: un tube à absorption ayant la longueur a 4.95 cm. attaché les fenêtres en quartz à deux côtés, un manomètre en mercure et un réservoir pour l'échantillon. Le C. O. T. est condensé dans ce réservoir par distillation en vide et ensuite l'appareil est complété par le détachement en fondant le tube de verre. Après avoir obtenu l'appareil, on fait modérer la tension du C. O. T. par l'abaissement de la température. L'extinction de cet échantillon est mesuré par l'appareil Spekker en utilisant comme source lumineuse une décharge d'étincelles entre électrodes de l'argent et de l'alliage de Cu-Zn-Al. Nous mettons ensuite les spectres obtenus sur une plaque photographique pour rayons cosmiques. Comme l'extinction du C. O. T. est très grande en région de la longueur d'onde vers 200 mμ, il est nécessaire de la mesurer sous basse tension de vapeur. On fait donc baisser la température de l'échantillon au-dessous de −10°, tandis qu'on maintient celle du tube à absorption à la température ordinaire.

Le changement de la température de l'absorption du C. O. T. dans la solution a déjà été publié,[3] tandis que notre présent mémoire donne les résultats éxécutés à l'état gazeux. Nous avons examiné le spectre d'absorption en utilisant le tube dont les deux côtés ont été joints avec les fenêtres en quartz fondues. Nous en avons changé la température entre 110° et 10°, mais avons trouvé peu d'influence de température à la bande d'absorption.

Les spectres d'absorption du C. O. T. et du $C_{10}H_{10}$ en solution sont tous obtenus au moyen du spectrophotomètre Spekker ou encore celui de Nutting appliqué spécialement en région visible. Nous avons étudié que la structure fine soit existée dans la bande d'absorption du C. O. T. et du $C_{10}H_{10}$, et l'avons examinée par la méthode de Hartley-Baly en utilisant comme source lumineuse l'étincelle sous l'eau

Table 1

Absorption lumineuse du C.O.T. et du $C_{10}H_{10}$.

| Composé | Dissolvant | λ, mμ | ε |
|---|---|---|---|
| C.O.T. | alcool méthylique | 280 | 350 |
| | alcool éthylique | 280 | 435 |
| | tétrachlorure de carbone | 288 | 320 |
| | heptane normal | 280 | 235 |
| | cyclohexane | 283 | 255 |
| $C_{10}H_{10}$ | alcool méthylique | 280 | 2100 |
| | | 230 | 26400 |
| | alcool éthylique | 280 | 2900 |
| | tétrachlorure de carbone | 280 | 2100 |
| | heptane normal | 280 | 2100 |

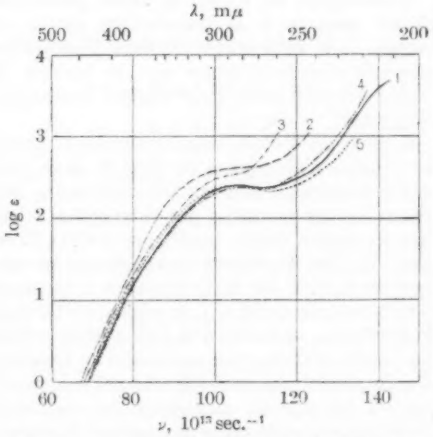


Fig. 3.—Spectre d'absorption du C. O. T. Les chiffres à la courbe montrent les dissolvants employés: 1, alcool méthylique; 2, alcool éthylique; 3, tétrachlorure de carbone; 4, heptane normal; 5, cyclohexane.

(3) A. Langseth et S. Broderson, *Acta Chemica Scandinavica*, **3**, 778 (1949); *Chem. Abst.*, **44**, 2369 (1950).

qui donne un spectre continu très fort dans la région ultraviolette voisine. Cet appareil de l'étincelle sous l'eau a été récemment construit à notre laboratoire[4]. Nous avons encore employé les plaques photographiques étant sensibilisées par l'amino-acide G ainsi que celles pour rayons cosmiques. Les résultats sont montrés dans la table 1 et par les figures 3 et 4.

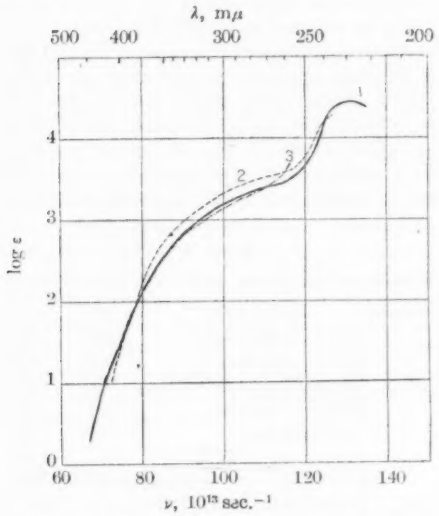


Fig. 4.—Spectre d'absorption du $C_{10}H_{10}$.

L'absorption du $C_{10}H_{10}$ à l'état gazeux est encore mesurée à la température élevée au moyen de la cuve employée dans l'expérience exécutée ci-dessus, parce que la tension de $C_{10}H_{10}$ est trop basse pour obtenir l'extinction moyenne.

Comme on le voit, dans la figure 3, toutes les courbes d'absorption du C. O. T. dans plusieurs dissolvants donnent un maximum vers 280 mμ et ne montrent pas l'absorption sélective en région visible tandis que le C. O. T. est jaune à l'état liquide et en solution. La couleur du C. O. T. est donc attribuée à l'absorption terminale étendue à la région visible dont le maximum se trouve à la région ultraviolette. La courbe d'absorption montrée à la longueur d'onde plus courte que celle vers 280 mμ monte jusqu'à 200 mμ en manquant de maximum d'absorption, mais on peut supposer l'existence d'absorption maxima vers 200 mμ par l'inclinaison de la courbe diminuée rapidement à la longueur d'onde un peu plus élevée que 200 mμ. La courbe d'absorption du C. O. T., soit à l'état gazeux, soit en solution, n'a pas la structure fine qu'on peut trouver à l'absorption du benzène.

Pour examiner la structure fine en absorption du C. O. T. à la température basse, nous avons photographié le spectre d'absorption du C. O. T. dissout dans l'heptane normal à la température d'environ −40°. Nous avons obtenu cette température basse par le refroidissement causé par la neige carbonique, mais nous n'y voyons pas de structure fine à pareille température.

L'absorption lumineuse du C. O. T. en solution[5] est influencée par le dissolvant employé, c'est-à-dire, la position de l'absorption maxima est seulement déplacée vers le rouge et son coefficient d'extinction grandit plus que l'état gazeux. Cet effet de dissolvant est le plus grand à l'alcool éthylique qui est le plus polaire dans nos dissolvants employés, et le moindre à l'heptane normal. L'extinction en solution de tétrachlorure de carbone est plus grande qu'on la prévoit au point de vue de sa polarité. Cette anormalité peut être aussi observée au cas de benzène dissous dans ce dissolvant.[6]

Le spectre d'absorption du $C_{10}H_{10}$ est semblable à celui du C. O. T. et n'a ni de structure fine, ni de bande sélective dans la région visible. Nous pouvons probablement conclure que les bandes d'absorption produites par le $C_{10}H_{10}$ à 280 mμ et à 230 mμ correspondent respectivement aux bandes de 280 mμ et de 200 mμ déjà montrées par C. O. T.. La couleur du $C_{10}H_{10}$ est jaune plus foncée que celle du C. O. T.. L'extinction moléculaire du $C_{10}H_{10}$ est 18 à la longueur d'onde 400 mμ, tandis que celle du C. O. T. est 8. L'extinction moléculaire dans la région ultraviolette est donnée à la table 1.

Nous avons encore étudié l'influence de l'iode sur le spectre d'absorption du C. O. T.. Le coefficient d'absorption du C. O. T. donne une tendance à croître dans sa solution de heptane normal et celle de tétrachlorure de carbone lorsqu'on y ajoute l'iode, savoir: dans la solution de heptane normal, quand la concentration du C. O. T. est $2.03\times10^{-3}$ mol/l. et celle d'iode est $1.97\times10^{-3}$ mol/l, l'extinction moléculaire $\varepsilon$ du C. O. T. change à 315 à la longueur d'onde 280 mμ. D'autre part, dans la solution de tétrachlorure de carbone, où la concentration du C. O. T. est $2.08\times10^{-3}$ mol/l. et celle d'iode est $1.98\times10^{-3}$ mol/l., du C. O. T. change de 250 à 430 à 280 mμ. Ces valeur de $\varepsilon$,

(4) T. Uémura, Y. Inamura, Y. Kondo et K. Morinaga, *J. Chem. Soc. Japan* **72**, 650 (1951).

(5) B. H. Eccleston, H. J. Coleman et N. G. Adams, *J. Am. Chem. Soc.*, **72**, 3868 (1950).

(6) V. Henri, *J. phys. et rad.*, **3**, 181 (1922).

influencées ne sont qu'environ le double de celle du C. O. T. qui ne contient pas l'iode. Ces résultats nous montrent le peu d'influence de l'iode sur le C. O. T.. Mais, au cas du benzène, la valeur $\varepsilon$ influencée par l'iode varie 30 fois plus que celle du cas sans l'addition de l'iode.[7] Cette conclusion nous conduit à penser que la structure électronique du C. O. T. est différente de celle des composés aromatiques comme le benzène et le toluène, malgré que le C. O. T. ait les liaisons doubles conjuguées dans sa molécule.

## Discussion

Nous avons déjà calculé la structure électronique du C. O. T.[2] et avons examiné le spectre d'absorption de la même substance. Nous n'exposons maintenant que son énergie de résonance. La chaleur de formation du C. O. T. est expérimentalement donnée par Prosen et ses colaborateurs.[8]

$$8C(\text{solide, graphite}) + 4H_2(\text{gaz}) = C_8H_8(\text{liquide})$$
$$\Delta H(298.16°\text{K}) = +60.82 \pm 0.32 \text{ kcal./mol}$$

On peut montrer la chaleur de formation aux états gazeux,

$$8C(\text{gaz}) + 4H_2(\text{gaz}) = C_8H_8(\text{gaz}) + 1352.9 \text{ kcal./mol}$$

car les énergies de liaison pour C−C, C=C et C−H sont respectivement données par 60.3 kcal., 102.9 kcal. et 87.13 kcal., la chaleur de formation pour $C_8H_8$ est donc dérivée à 1350 kcal. en utilisant celles ci-dessus exposées. L'énergie de formation et celle de liaison. Cette énergie de résonance montre la valeur de 7-8% de celle de benzène.

Nous avons fait la calculation de l'énergie de résonance du C. O. T. par deux méthodes approximatives, une la méthode de HLSP,[9] et l'autre, elle de HMH.[10]

(1) Méthode de HLSP

$$\alpha = \int \Psi_1(1)\Psi_2(2)\Psi_3(3)\Psi_4(4)\ldots. \mathrm{H}\tilde{\Psi}_1(2)\tilde{\Psi}_2(1)\tilde{\Psi}_3(3)\tilde{\Psi}_4(4)\ldots.\mathrm{d}\tau$$

$$\alpha' = \int \Psi_1(1)\Psi_2(2)\Psi_3(3)\Psi_4(4)\ldots. \mathrm{H}\tilde{\Psi}_1(1)\tilde{\Psi}_2(3)\tilde{\Psi}_3(2)\tilde{\Psi}_4(4)\ldots.\mathrm{d}\tau$$

Si on prend 1.5 e.V. pour la valeur de $\alpha$, on a pour l'énergie de résonance suivante:

Table 2

| | $\alpha'=0.25\alpha$ | $\alpha'=0.3\alpha$ | $\alpha'=0.35\alpha$ |
|---|---|---|---|
| énergie de résonance | 1.73 kcal. | 2.47 kcal. | 3.46 kcal. |

Comme on voit dans la table précédente, plus l'énergie commutative grandit, plus l'énergie de résonance augmente.

(2) Méthode de HMH[11]

$$8 \mid \varepsilon_{(C_8H_8)} \mid = 8\varepsilon_E \frac{1}{\sigma}(Q+R_1) = 23.606 \text{ e. V.}$$

$$\mid \varepsilon_{(\text{C.O.T.})} \mid = \mid 2\epsilon_1 + 4\epsilon_2 + 2\epsilon_3 \mid$$
$$= 2\frac{1}{\sigma_1}\{Q - R_1 - R_7\} + 4\frac{1}{\sigma_2}\left\{Q + \frac{1}{S}R_1 + \frac{k}{S}R_7\right\}$$
$$+ 2\frac{1}{\sigma_3}\{Q + R_1 + R_7\} = 23.735 \text{ e. V.}$$

où

$$\varepsilon_i = \int \varphi_i H \varphi_i^* \,\mathrm{d}\tau$$

$$Q = -\int \mathrm{I}\, H\, \mathrm{I}\,\mathrm{d}\tau$$

$$R_1 = -\int \mathrm{I}\, V_1\, \mathrm{II}\,\mathrm{d}\tau$$

$$R_7 = -\int \mathrm{I}\, V_7\, \mathrm{VIII}\,\mathrm{d}\tau$$

comme les facteurs normalisés:

$$\sigma_1 = 1 + d_1 + d_7 + 2d_2$$
$$\sigma_2 = 1 + \frac{1}{S}d_1 + \frac{k}{S}d_7$$
$$\sigma_3 = 1 + d_1 - d_7 - 2d_2$$
$$\sigma = 1 + d_i$$

les intégrales sont les suivants:

$$d_1 = \int \mathrm{I}\ \mathrm{II}\,\mathrm{d}\tau$$

$$d_2 = \int \mathrm{I}\ \mathrm{III}\,\mathrm{d}\tau$$

$$d_7 = \int \mathrm{I}\ \mathrm{VIII}\,\mathrm{d}\tau$$

L'explication des signes utilisés dans ces équations se trouve dans notre mémoire précédent.[10]

Par cette calculation l'énergie de résonance

(7) H. A. Benesi et J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2707 (1949); R. S. Mulliken, *ibid.*, **72**, 600 (1950).
(8) E. J. Prosen, W. H. Johnson et F. D. Rossini, *J. Am. Chem. Soc.*, **69**, 2068 (1947); **72**, 626 (1950).
(9) La méthode de HLSP signifie l'abréviation de celle de Heitler-London-Slater-Pauling.
(10) La méthode de HMH est ainsi celle de Hund-Mulliken-Hückel.
(11) ce bulletin, **23**, 168 (1950).

devient à peu près 3 kcal., qui est environ 8% de celle de benzène.

C'est entendu que le C. O. T. n'a guère le caractère aromatique en considerant du point de vue de l'énergie de résonance ainsi les autres propriétés physico-chimiques. Les spectres d'absorption du C. O. T. et du $C_{10}H_{10}$ sont semblables l'un et l'autre et on en conclut que les deux composés ont aussi la structure pareille. Nous continuons encore à étudier les propriétés du $C_{10}H_{10}$ et nous avons l'intention de publier bientôt le résultat de nos recherches.

### Résumé

(1) Nous avons mesuré les spectres d'absorption du C. O. T. et du $C_{10}H_{10}$ à l'état gazeux et en solution.

(2) Deux bandes d'absorption se trouvent dans la région ultraviolette et elles ne donnent pas de structure fine.

(3) Les deux bandes du $C_{10}H_{10}$ correspondent à celles du C. O. T., mais celles-là sont plus bathochromiques et, en même temps, plus hyperchromiques que celles-ci.

(4) L'effet de dissolvant du C. O. T. par l'alcool éthylique est le plus grand parmi tous les dissolvants employés.

(5) Le coefficient d'absorption du C. O. T. à la longueur d'onde à 280 m$\mu$ croît un peu lorsqu'on y ajoute l'iode.

En terminant ce compte-rendu, nous avons à exprimer nos sincères remerciements au professeur S. Murahashi et au Dr. N. Hagiwara à l'Institut de Recherche scientifique et industrielle de l'Université d'Osaka, pour nous avoir offert les matières utilisées dans nos recherches actuelles, au Dr. S. Shida qui nous a bien encouragé pendant nos expériences, et, en même temps, au ministère de l'Instruction publique qui nous a aidés en se chargeant des frais de nos recherches.

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# On the Mono-molecular Layer of $\alpha$-Aminolauric Acid Polymer

Keiichi EDA and Yukio MASUDA

(Received March 17, 1951)

### Introduction

The researches which have been made on the monolayers of various high polymers, natural and synthetic, for the past twenty years gave many valuable suggestions on the chemical structures of these polymers, above all, of natural proteins.

This short paper describes the results of surface pressure and potential measurements on films of $\alpha$-aminolauric acid polymer which was synthesized as a protein-like high polymer. This polymer was chosen because it contains nonpolar lauric acid residue only as the side chain and electrical properties of the film are mainly ascribed to that of its polypeptide portions.

### Experiment

Force-area relations were measured with a Langmuir-Adam surface balance of which sensitivity is 0.3 dyne. The surface potential was measured simultaneously with a dynamic electrometer.[1] The brass tray used was heavily coated with paraffine. $\alpha$-Aminolauric acid polymer was synthesized in the laboratory of Dr. H. Tani and Dr. J. Noguchi by the method of N-carbonic acid anhydride of amino acid. The molecular weight determined by the osmotic pressure measurement was 172,000, and the mean polymerization degree was 870.[2] It was spread on the water surface from benzene solution. Various $p$H solutions, and ammonium sulfate solutions were used as the substrates. All experiments were done at room temperature which was never above 15° or below 10°.

### Results

Fig. 1 gives the results on distilled water, on $N/100$ HCl solution, and on $N/100$ NaOH solution. Full curves show the surface pressure, $F$, and the broken lines show the surface

(1) Cf., Rosenfeld and Hoskins, *Rev. Sci. Inst*, **16**, 343 (1945).

(2) H. Tani and J. Noguchi, *Jour. High Polymers, Japan*, **8**, 51 (1951).

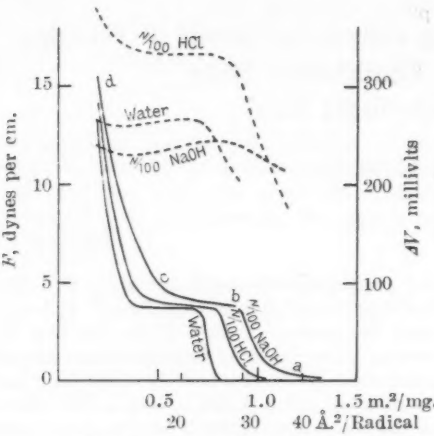


Fig. 1.—Various *p*H solutions.

potential change, $\Delta V$, due to the films.

The whole shape of the curve resembles that of the transition curve shown by fatty acids. Each of the surface pressure area curves consists of three portions, a-b, b-c, and c-d. As the films on dilute solutions are highly compressible in the region, b-c, the curves are almost completely flat. The surface potential values fluctuate at large areas, but are stabilized at the concentration at which the surface pressure appeared (point a). On further compression lauric acid residues rise out of water surface and the surface potential increases rapidly up to a value at point b. It may be considered that in the highly compressible state, b-c, some transitions occur in the polypeptide main chain to form more compact structure. The nearly constant value of the surface potential in this region means that the compact form has a smaller normal dipole moment. The area decreased further, the surface pressure increases rapidly (point c). This sharp rise in surface pressure with compression indicates that at this point all the lauric acid residues are out of water and are packed closely as possible. The cross sectional area of a lauric acid radical is about 20 Å.² or less at zero compression. The effect of the hydroxyl ions on the spreading of the polypeptide is greater than that of the hydrogen ions. The values of the vertical component of the dipole moment per radical at point b are given below,

| | | |
|---|---|---|
| on distilled water | $2.0\times10^{-19}$ e.s.u. per radical | |
| on $N/100$ HCl | 2.8 | „ |
| on $N/100$ NaOH | 2.3 | „ |

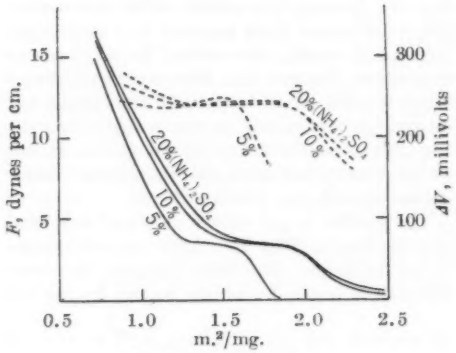


Fig. 2.—Salt solutions.

Fig. 2 exhibits the effect of salt concentrations of the substrate on the spreading. It seems probable that the large areas on the substrates of the increased concentrations are due to the adsorption of the salt ions.

The authors are grateful to Prof. B. Tamamushi for his kind guidance, and besides, to Dr. H. Tani and Dr. J. Noguchi for the provision of the polymer sample used in this work. A part of the expense of this study was defrayed from the Scientific Research Grant of the Ministry of Education.

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# On the Possibility of Concentrating Colloid by Means of Freezing at the Sedimentation Equilibrium State Attained in a Centrifugal Field

By Tominosuke KATSURAI

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In this note a suggestion has been made that the freezing of a colloid at the sedimentation equilibrium state attained in a centrifugal field could possibly be utilized as a means to concentrate the colloid. The argument is confined to the case in which the dispersion medium is water, and in which the concentration and molecular weight of the colloid, as well as the concentration of the electrolyte present in the colloid, are small.

The colloid is put into a cell and subjected to centrifuging (Fig. 1). After the sedimentation equilibrium has been reached, the temperature is lowered and the colloid in the cell

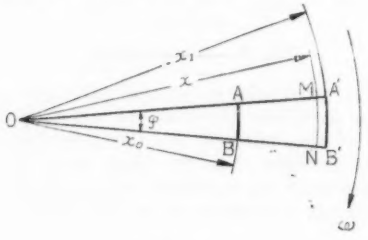


Fig. 1.

is frozen. Centrifuging is then stopped and the frozen colloid is taken out of the cell and the part near the bottom is removed. This is put to stand at a temperature slightly above zero and the frozen colloid is brought back to a sol which has a concentration greater than the initial one. Starting from the ample quantity of the colloid and by repeating the procedure, it is possible to get a colloid of very high concentration, if the colloid does not change by being subjected to the freezing-thawing treatment.

There are two factors which might influence the course of freezing of the colloid. They are hydrostatic pressure and concentration gradient. We know that the freezing point of water is lowered under pressure. The hydrostatic pressure of the colloid is the smallest at the top of cell AB and increases with $x$. Thus, when the temperature is lowered in equilibrium, ice formation will start at the top and then proceeds gradually along $Ox$. The fact that ice is lighter than water will also favor the tendency. In a dilute solution, the freezing point lowering is proportional to concentration. From this fact we understand that the freezing point of the colloid is the highest at the top AB and that it becomes lower with the increase of $x$. Thus, both the hydrostatic pressure and the concentration gradient favor the ice formation from the top AB toward the bottom A'B', acting in the tendency to enhance the concentration gradient.

How far the colloid is concentrated by this procedure can be estimated as follows: Let us consider the colloid in AA'B'B. The thickness of cell is taken as unity. The concentration gradient in the sedimentation equilibrium is given by

$$\frac{c}{c_0}=\frac{\alpha(x_1^2-x_0^2)}{e^{\alpha x_1^2}-e^{\alpha x_0^2}}\cdot e^{\alpha x^2}, \qquad (1)$$

where $c$=concentration of colloid, $c_0$=initial concentration of colloid, $x$=distance from the axis of rotation, $x_0$=OA, $x_1$=OA', $\varphi$=sector angle, $s$=sedimentation constant of colloid, $D$=diffusion constant of colloid, $\omega$=angular velocity, and $\alpha=\dfrac{s\omega^2}{2D}$ [1].

If we could take out the colloid contained in the part MA'B'N near the bottom of cell without disturbing the concentration gradient, then we have a colloid having a concentration greater than $c_0$. As a measure of the increase of the concentration, we make use of the *local average concentration*, a function of $x$, defined by

$$\bar{c}(x)=\frac{\text{total amount of colloid in MA'B'N}}{\text{volume of MA'B'N}},$$

(1) S. Oka, *Proc. Phys.-Math. Soc. Japan*, **18**, 522(1936). This formula was derived as the solution of a special case ($\partial c/\partial t=0$) of Lamm's differential equation of ultracentrifuging. A formula essentially the same, but without explicit use of sedimentation constant and diffusion constant, was given by Rinde before the publication of Lamm's equation. (Cf. H. Rinde, Dissertation, p. 176 (Upsala, 1928)). Oka's equation is used herewith for the sake of convenience.

or
$$\bar{c}=\frac{\int_0^{\varphi}\int_r^{x_1} cx\,dx\,d\varphi}{\frac{1}{2}\varphi(x_1^2-x^2)}. \qquad (2)$$

This gives the average concentration of the colloid in MA'B'N at sedimentation equilibrium, and the ratio $\bar{c}/c_0$ gives the relative increase of the concentration. By means of (1), we obtain

$$\frac{\bar{c}}{c_0}=\frac{x_1^2-x_0^2}{e^{\alpha x_1^2}-e^{\alpha x_0^2}}\cdot\frac{e^{\alpha x_1^2}-e^{\alpha x^2}}{x_1^2-x^2}. \qquad (3)$$

We see from this that

$$[\bar{c}]_{x=x_0}=c_0,\quad \lim_{x\to x_1}[\bar{c}]=[c]_{x=x_1}$$

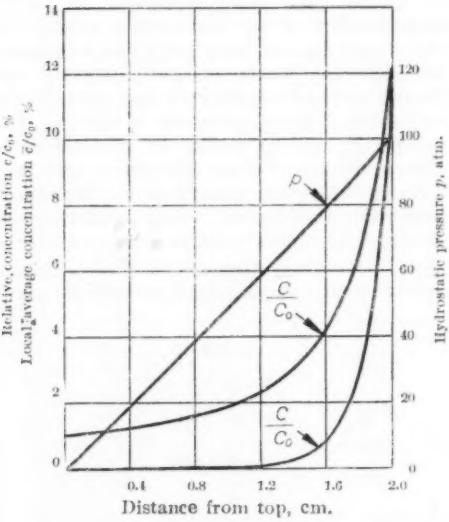


Fig. 2.

and $\bar{c}>c$ for $x_1>x>x_0$.

For the sake of illustration, an example is given. Put $M=10{,}000$, $V=0.75$, $\rho=1.00$, $x_0=5.0$ cm., $x_1=7.0$ cm., and r. p. m.$=30{,}000$ or $\omega=3{,}140$, where $M$=molecular weight, $V$=partial specific volume, and $\rho$=density. In order to use the formula (3), it is necessary to know the value of $s/D$. We find this by means of the sedimentation velocity formula

$$\frac{s}{D}=\frac{M(1-V\rho)}{RT},$$

where $R$ and $T$ have their usual meanings. Using the above data and assuming that $T=288$ we have $s/D=1.044\times10^{-7}$. The results obtained by using this value are given in Fig. 2.

The hydrostatic pressure $p$ in the cell is given as a function of $x$ by the following relation

$$p=\frac{\rho\omega^2}{3}\left(x^3-\frac{x_0^3}{x}\right). \qquad (4)$$

The values of $p$ calculated by this formula is also given in Fig. 2. From the Clausius-Clapeyron equation we understand that for the ice at 0°, the rate of freezing point lowering is $-0.0076°$ per atmosphere. We see from Fig. 2 that the difference of freezing points at AB and A'B' is about 0.8° corresponding to the hydrostatic pressure difference 101 Atm.

In conclusion, the author wishes to express his cordial thanks to Professor Ole Lamm of Kungl. Tekniska Högskolan, Stockholm for his valuable remarks.

*Scientific Research Institute Ltd.,*
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# Studies on Amino-hexoses. II. The Mechanism of the Formation of So-called Chitose from Glucosamine

By Yoshio MATSUSHIMA

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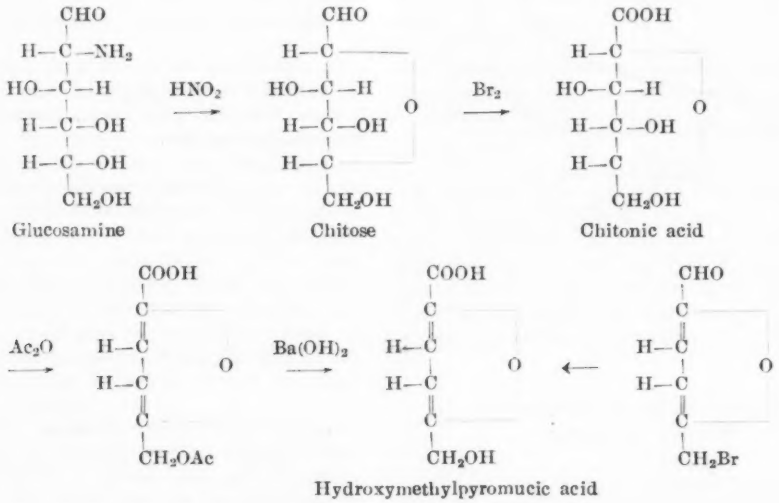
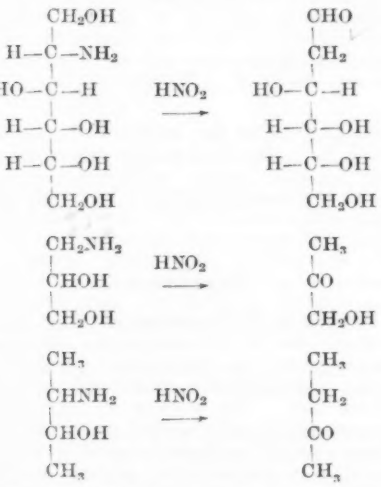
The reaction of nitrous acid upon glucosamine (2-amino-2-desoxyglucose) does not proceed, as expected from our "common" knowledge, to the production of glucose or mannose but to the production of so-called chitose. Fischer and Tiemann[1] obtained an acid which they called chitonic acid as its calcium salt by the bromine oxidation of the sugar-like substance which was formed from glucosamine by the action of nitrous acid and named by them chitose. Later, Fischer and Andreae[2] treated chitonic acid with acetic anhydride and sodium acetate and obtained hydroxymethyl-pyromucic acid, the constitution of which was confirmed by Haworth, Hirst and Nicholson[3] through its preparation from ω-bromo-5-methyl-furfural. Fischer and Andreae[2] proposed the 2,5-anhydro-hexose structure for chitose from the elementary composition of chitonic acid and the reactions mentioned above which can be summerized as follows:

The "abnormal" behavior of glucosamine toward nitrous acid caused several workers to repeat the Fischer's experiment and the complicated results have been reported. Armbrecht[4] believed that he obtained a hexosazone which was different from glucosazone, but the formation of osazone must be impossible if chitose has the structure mentioned above. Zechmeister and Toth[5] reported the formation of glucose and they attributed the non-fermentability of the deamination mixture to the co-existence of some inhibitory substance. Schorigin and Makarowa-Semljanskaya[6] approved of the Fischer's result and obtained the crystalline diphenylhydrazone of chitose. The complexity of the results let the authors of the text-books of sugar chemistry state that "Unsere bisherigen Kenntnisse von der chitose sind recht lueckenhaft. Auch Zweifel an der Einheitlichkeit des Produktes erscheinen berechtigt,"[7] or "Die Chemie der Chitose bedarf jedoch noch einer eingehenden Bearbeitung."[8]

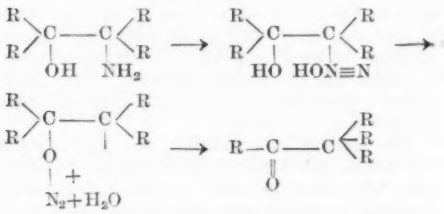



(1) E. Fischer and F. Tiemann, *Ber.*, **27**, 138 (1894).
(2) E. Fischer and F. Andreae, *Ber.*, **36**, 2587 (1903).
(3) W. N. Haworth, E. L. Hirst and V. S. Nicholson, *J. Chem. Soc.*, **1927**, 1513.
(4) W. Armbrecht, *Biochem. Z.*, **95**, 108 (1919).
(5) L. Zechmeister and G. Toth, *Ber.*, **66**, 522 (1933).
(6) P. Schorigin and N. N. Makarowa-Semljanskaya *Ber.*, **68**, 965 (1935).
(7) Tollens-Elsner, "Kurzes Handbuch der Kohlenhydrate", 1935, S. 521.
(8) F. Micheel, "Chemie der Zucker und Polysaccharide," 1939, S. 161.

However, the author's deamination experiment on glucosaminol, the hydrogenated product of glucosamine, and on some model substances, together with the search into literatures enabled him to put a reasonable interpretation upon the formation of chitose from glucosamine. The author found that glucosaminol, when treated with nitrous acid, did not produce any trace of sorbitol nor mannitol. The reaction mixture exhibited a reducing action upon Fehling's reagent and crystalline diphenylhydrazone was isolated from it. This was identified with the diphenylhydrazone of 2-desoxy-glucose. The experiments on two model substances proceeded equally on the same line with glucosaminol. Thus, 1-amino-propane-diol-(2, 3) produced acetol and 2-amino-butanol-(3) produced methylethylketone when treated with nitrous acid.



McKenzie[9],[10] first observed the "abnormal" reaction of nitrous acid upon $\alpha$-hydroxyl-amines and named the reaction "semi-pinacolinic deamination" and explained the reaction by the following scheme.

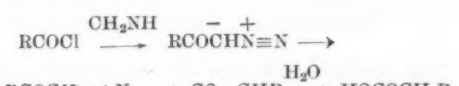


(9) A. McKenzie, *J. Chem. Soc.*, **123**, 79 (1923).
(10) A. McKenzie, *J. Chem. Soc.*, **125**, 844 (1924); cf. A. McKenzie and W. S. Dennler, *J. Chem. Soc.*, **125**, 2105 (1924); A. McKenzie and A. K. Mills, *Ber.*, **62**, 284 (1929); A. McKenzie and A. D. Wood, *Ber.*, **71**, 358 (1938).

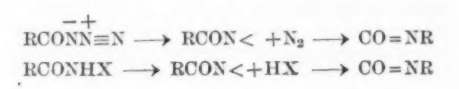
Several workers[11] have been engaged in the works of this line and the mobility of radicals has been discussed.

On the other hand, the "abnormal" reaction of nitrous acid upon common amines has been observed for a long time. Meyer and Forster[12] reported the production of iso-propyl alcohol beside $n$-propyl alcohol when $n$-propyl amine was deaminated with nitrous acid. Freund and Schoenfeld[13] observed the production of olefinic hydrocarbon $CH_2=C(CH_3)C_6H_{13}$ and tertiary alcohol $(CH_3)_2C(OH)C_6H_{13}$ from the amine $NH_2CH_2CH(CH_3)C_6H_{13}$. According to Levy and Gallais[14] $Ph_2CHCH_2NH_2$ gives stilben $PhCH=CHPh$. Enlargement of the ring is reported by Wallach[15] and Ruzicka[16] when amino-methyl cyclo-paraffin is treated with nitrous acid.

The author's interpretation of these "abnormal" reactions originates in the Arndt-Eistert's[17] synthesis of carboxylic acid homologues:



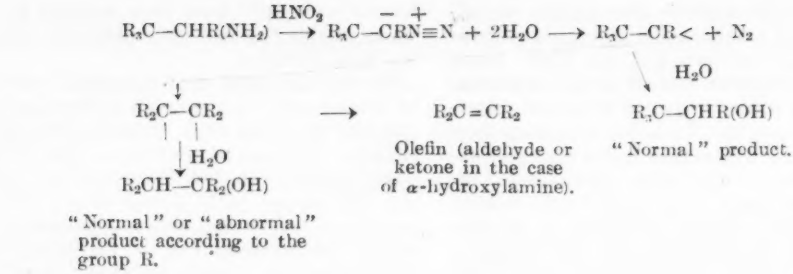
The reaction mechanism has an analogy in the Curtius' degradation of acid azide or in the Hofmann's degradation of acid amide.

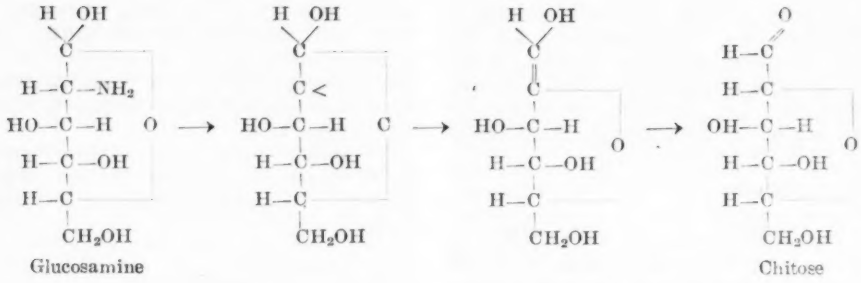


In these reactions the intermediate bivalent radicals cause the rearrangements of atomic groups. The reactions of amines with nitrous acid can also be interpreted in the light of the same reaction mechanisms which are summerized as follows (the upper schema of p. 146).

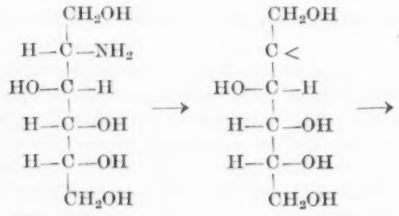
McKenzie[9] has already pointed out the similarity between glucosamine and $\alpha$-hydroxyl-amines in respect of "unusual" behavior toward nitrous acid but he could not interpret explicitly the formation of 2, 5-anhydro-ring in chitose. The author offers the following mechanism for the formation of chitose.

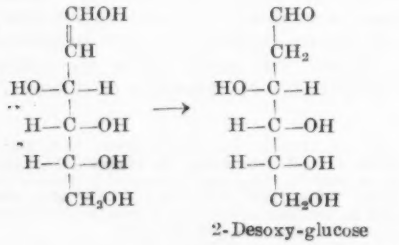
(11) M. Tiffeneau and J. Lévy, *Compt. rend.*, **183**, 969 (1926); *C. A.*, **21**, 908 (1927); M. Migita, This Bulletin **3**, 308 (1928); S. Kanao and T. Yaguchi, *J. Pharmac. Soc. Japan*, **48**, 252 (1928); A. K. Mills, *J. Chem. Soc.*, **1934**, 1565; M. Tiffeneau, J. Levy and E. Détz, *Bull. Soc Chim.*, (5) **2**, 1871 (1935); *C. A.*, **30**, 1781 (1936).
(12) V. Meyer and F. Forster, *Ber.*, **9**, 535 (1876).
(13) M. Freund and F. Schoenfeld, *Ber.*, **24**, 3350 (1891).
(14) J. Lévy and P. Gallais, *Bull. Soc. Chim.*, **43**, 862 (1928); *C. A.*, **22**, 4504 (1928).
(15) O. Wallach, *Ann.*, **353**, 325 (1907).
(16) L. Ruzicka, *Helv.*, **9**, 399 (1925).
(17) F. Arndt and B. Eistert, *Ber.*, **68**, 200 (1935).




The pyranoid structure of glucosamine has been established by Irvine and Hynd.[18] The intermediate bivalent radical causes the rearrangement of lactol ring, thus forming the furan ring of chitose. Glucosaminol converts into 2-desoxy-glucose following the same reaction mechanism.




The author emphasizes with Berk and Hermans[19] that the replacement of amino-group by hydroxyl is merely one of the probable reaction courses when primary amines of the type >CHNH$_2$ are treated with nitrous acid.

## Experimental

**Preparation of Glucosaminol.**—High pressure hydrogenation of glucosamine in small scale has been reported by Karrer and Meyer.[20] The author hydrogenated a considerable quantity of glucosamine. The solution of 130 g. D-glucosamine hydrochloride in 500cc. of water added with Raney's nickel catalyser prepared from 50 g. of the alloy is heated under shaking at 100° for several hours until the hydrogen pressure becomes constant (initial pressure, 80 atm.). The reaction mixture is filtered from nickel and concentrated *in vacuo*. The resulting thick syrup is added with 400 cc. of absolute alcohol and the seed crystals. Crystalization takes place immediately. The yield of raw crystals of glucosaminol hydrochloride which show a trace of reducing action amounts to 122 g. 40 g. of raw crystals is dissolved in 40 cc. of water and 160 cc. of absolute alcohol is added under vigorous agitation. Colorless fine crystals precipitate immediately which weigh 24.5 g. and melt at 159-160°.

The method of obtaining free base described by Karrer and Meyer[20] which consists in shaking the hydrochloride with alcoholic diethylamine solution is tedious and incomplete. The author proceeded as follows:

(18) J. C. Irvine and A. Hynd, *J. Chem. Soc.*, **101**, 1128 (1912).

(19) J. Berk and P. H. Hermans, *Chem. Weekblad*, **22**, 270 (1925); *C. A.*, **19**, 2473 (1925).

(20) P. Karrer and J. Meyer, *Helv.*, **20**, 626 (1937).

10 g. of the hydrochloride is dissolved in 10 cc. of water and 5 g. of diethyl amine is added slowly. After adding 150 cc. of alcohol, the rubbing of the wall accelerates the growth of crystals. The colorless crystals of the free base thus obtained are quite free from chlorine and melt at 131-132°. The yield amounts to 75% of theory.

**Deamination of Glucosaminol.**—6.0 g. of glucosaminol (free base) dissolved in 50 cc. of water is added with 3 g. of sodium nitrite dissolved in 50 cc. of water and then with 3 cc. of acetic acid. Evolution of nitrogen gas ceases after over-night standing at room temperatures. The reaction mixture is concentrated *in vacuo* and is added with 2 g. of diphenylhydrazine dissolved in 5 cc. of alcohol. After an over-night standing the rubbing of the wall accelerates crystalization. The crystals thus obtained weigh 2.6 g. and melt at 175-177°. 0.2 g. of the same substance is recovered from the mother liquor. The substance which melts at 178-179° after being recrystalized twice from 96% alcohol shows no melting point depression when mixed with the diphenylhydrazone of 2-desoxyglucose which is prepared from D-glucal following the method of Bergmann, Schotte and Lechinsky.[21] Analyses give the following results:

| | |
|---|---|
| Found: | C, 65.56; H, 6.74. |
| Calcd. for $C_{18}H_{22}O_4N_2$: | C, 65.44; H, 6.71. |

**Preparation of 1-Amino-propane-diol and 2-Amino-butanol-(3).** (a) 1-Amino-propane-diol was prepared following the method of Knorr[22] taking account of the report of Hirata.[23] The substance boiling at 140-141°/9 mm. in redistillation is colorless viscous liquid which has no reducing action toward Fehling's reagent or ammoniacal silver solution.

(b) 2-Amino-butanol-(3) was prepared following the method of Strauss[24] which was somewhat modified.

Diacetyl monoxime is reduced with sodium amalgam under cooling with ice and salt in acid conditions. The reaction mixture is made alkaline and extracted with ether in a automatic apparatus for 5 days. The substance boiling at 53.5-55.5°/7 mm. in redistillation is colorless viscous liquid which has a pyridine-like odor. The yield is 2.3 g. from 5 g. of diacetyl monoxime.

**Deamination of 1-Amino-propane-diol and 2-Amino-butanol-(3).** (a) 10 g. of 1-amino-propane-diol is dissolved in 50 cc. of water and the solution of 8.5 g. sodium nitrite in 10 cc. water is added. 25 cc. of 6 *N*-sulfuric acid is dropped into the mixture under stirring and ice-water cooling. After letting it stand for 4.5 hours at room temperatures hydrogen gas is passed until no trace of nitrous acid remains. Van Slyke amino determination carried out with a portion of the reaction mixture reveals that 2.8 g. of the starting amino-alcohol remains intact. The reaction mixture which exhibits now a strong reducing action upon Fehling's reagent or upon ammoniacal silver solution is neutralized with barium carbonate and the filtrate from barium sulfate is divided into two equal portions. One is treated with phenylhydrazine acetate and the other with semicarbazide. Precipitation takes place immediately in each case and the yield of raw phenylosazone of acetol melting at 137° with decomposition is 2.28 g. and that of semicarbazone melting at 197.5° with decomposition is 1.09 g. The yield of both derivatives of acetol corresponds to about 20% of the starting amino-alcohol consumed. The osazone melts at 146.5-147° with decomposition when once recrystalized from alcohol. The analyses give the following results:

| | |
|---|---|
| Found: | C, 71.75; H, 6.47; N, 22.42. |
| Calcd. for $C_{15}H_{16}N_4$: | C, 71.40; H, 6.39; N, 22.21. |

The semicarbazone melts at 197-198° with decomposition when once recrystalized from water. The analyses give the following results:

| | |
|---|---|
| Found: | C, 36.54; H, 7.21; N, 32.56. |
| Cald. for $C_4H_9O_2N_3$: | C, 36.66; H, 6.91; N, 32.04. |

(b) 1.06 g. of 2-amino-butanol-(3) is dissolved in 10 cc. of water and the solution of 1.4 g. of sodium nitrite in 15 cc. of water is added. 3 cc. of acetic acid is dropped at room temperatures into the mixture under stirring. After an over-night standing the mixture is neutralized with sodium hydroxide to a *p*H value of 5 and distilled to about 80% of the whole. The distillate upon treatment with dimedone solution gives a precipitate which may be isobutylaldomedone[25] but can not be identified owing to the small amount of the material. The mixture is again distilled and the distillate is now added with acetic solution of *p*-nitrophenylhydrazine. Precipitation takes place immediately. The yellow crystals thus formed weigh 0.88 g. and melt at 90-100°. After being recrystalized three times the specimen melts at 124-124.5° alone or at 125-126° with the authentic specimen of *p*-nitrophenylhydrazone of methyl ethyl ketone which melts at 127.5-128°. Analyses give the following results:

| | |
|---|---|
| Found: | N, 20.37. |
| Calcd. for $C_{10}H_{13}C_2N_3$: | N, 20.28. |

The author expresses his gratitudes for the guidance of Prof. Dr. S. Akabori and for the assistance from Mr. K. Okawa and Mr. T. Ikenaka.

*Science Department, Osaka University, Osaka*

(21) M. Bergmann, H. Schotte and W. Lechinsky, *Ber.*, **55**, 165 (1922).
(22) L. Knorr and E. Knorr, *Ber.*, **32**, 750 (1899).
(23) Y. Hirata, K. Inukai and T. Tsujiuchi, *J. Chem. Soc. Japan*, **69**, 59 (1948).
(24) E. Strauss, *Ber.*, **33**, 2827 (1900).
(25) S. Akabori, *J. Chem. Soc. Japan.*, **59**, 1132 (1938).

# Equilibrium of the $CO_2$-$NH_3$-Urea-$H_2O$ System under High Temperature and Pressure. I. Equilibrium Pressure of Reaction in Urea-Synthesis from Ammonia and Carbon Dioxide

By Schōhachi KAWASUMI

(Received December 18, 1950)

## Introduction

In general, it is said that a content in a reaction vessel for the synthesis of urea from ammonia and carbon dioxide under high temperature and pressure is separated into two phases of melted solution and vapor.[1] But no one, so far as I know, has succeeded in analyzing plainly the equilibrium between the two phases in spite of the importance of industrial production of urea.

The writer has studied the equilibrium between the two phases of the $CO_2$-$NH_3$-Urea-$H_2O$ system under high temperature and pressure.

The relations between the temperature and the equilibrium pressure of the reaction have been studied by several investigators.[1~4] The reported values as shown in Fig. 1 are divergent, while the experimental values[5] of the decomposition pressure of ammonium carbamate in the temperature range 10° to 80° are relatively fixed.

This paper covers a study of the equilibrium pressure of the reaction, in which loading mol ratio of carbon dioxide to ammonia is one by two, at the temperature range 130° to 170°, that is to say, in the absence of an excess of either reactant.

The experimental results showed that the equilibrium pressure depends upon the loading density or ratio of the weights of the materials to the total volume of the reaction vessel at a given temperature. From this experimental facts the writer discusses the relations among the temperature, the equilibrium pressure and the loading density.

## Experiment

The apparatus used for pressure measurements is shown in Fig. 2. The reaction vessel is made of steel with lead-lining and capacity is approximately 800 cc. For measuring pressure, the mercury trap of 20 cc. volume was fixed between the reaction vessel and the Bourdon pressure gauge to prevent condensation of ammonium carbamate in it. The reaction vessel and the mercury trap were both dipped in a thermoregulated oil bath and heated at a given temperature for 20 to 24 hours. The container was loaded with crystalline ammonium carbamate or equi-molal mixture of urea and water.

Ammonium carbamate was prepared from refined gaseous carbon dioxide and ammonia in a glass vessel at ordinary temperature and pressure.

The same equilibrium pressure was obtained from the carbamate side of the reaction and also from the urea-water side on the same basis of initial loading density. Therefore, the equilibrium

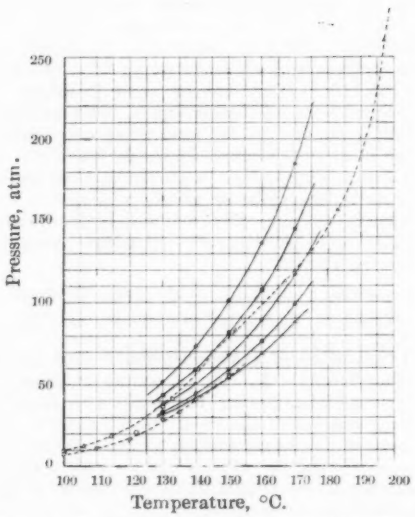



Fig. 1.—Pressure-temp. curves of the $CO_2$-$NH_3$-Urea-$H_2O$ system. Loading density g./cc. of the present measurement: ◆, 1.0; ■, 0.8; ▼, 0.6; ●, 0.4; ▲, 0.2. Results given by other investigators: △, Briner [2]; □, Fichter and Becker [3]; ○, Matignon and Frejacques [1]; ▽, Tokuoka [4].

(1) Matignon and Fréjacques, *Compt. rend.*, **171**, 1003 (1920); *Bull. soc. chim.*, **31**, 394 (1922).
(2) Briner, *J. chim. phys.*, **4**, 266 (1906).
(3) Fichter and Becker, *Ber.*, **44**, 3473 (1911).
(4) Tokuoka, *J. Agr. Chem. Soc. Japan*, **11**, 174 (1935).
(5) Egan, J. E. Potts and G. D. Potts, *Ind. Eng. Chem.*, **38**, 454 (1946).

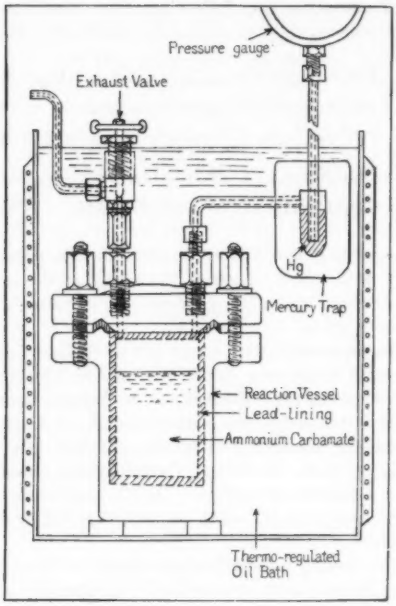



Fig. 2.—Apparatus for measuring the equilibrium pressure of the $CO_2$-$NH_3$-urea-$H_2O$ system. I.

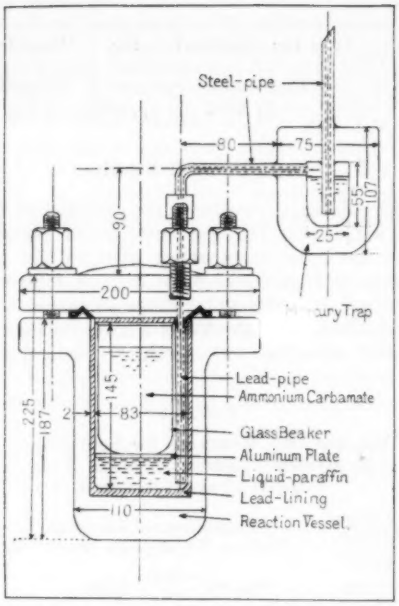



Fig. 3.—Apparatus for measuring the equilibrium Pressure of the $CO_2$-$NH_3$-Urea-$H_2O$ system. II.

pressure is constant regardless of the kinds of starting materials at a given temperature and loading density.

In the preliminary experiments, the equilibrium pressure was measured after eliminating a small amount of residual air in the reaction vessel by a vacuum pump at ordinary temperature in the beginning of the experiment and then the last residual air together with carbamate decomposition gas at 100°. But in the other experiments in which these procedures were omitted, the same results were also obtained. Therefore, as the effect of residual air for the equilibrium pressure is very small, these procedures were omitted.

The writer measured the equilibrium pressure in the apparatus of Fig. 3 which is more corrosion-resistant than that of Fig. 2. The following device was made so that corrosive gas might not touch the mercury trap and the steel-pipe connecting between the former and the reaction vessel. Because both of the mercury trap and the steel trap have no lead-lining. The apparatus of Fig. 3 has a lead-pipe of inner diameter 3 mm. and length 14 cm., jointing to the cover of the reaction vessel and reaching almost to the bottom of the vessel where 60 cc. of liquid paraffin is charged. Ammonium carbamate is loaded in a glass beaker through an aluminum plate on the liquid paraffin. At a high temperature, carbamate decomposition gas compresses the liquid paraffin which arrives at the mercury-trap through the lead-pipe and steel-pipe. Therefore the gas in the apparatus touches only the glass and lead wall, aluminum plate and liquid paraffin, and no steel wall.

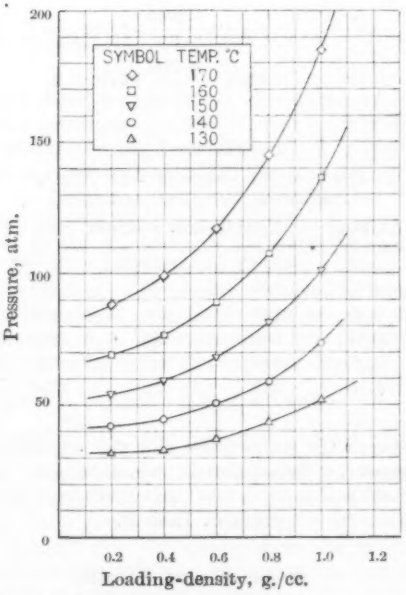



Fig. 4.—Equilibrium pressure-loading density curves of the $CO_2$-$NH_3$-Urea-$H_2O$ system.

The experimental results of this apparatus were of the same values as those obtained in the experiments of the apparatus of Fig. 2. Therefore, the effect of corrosion of carbamate decomposition gas for the equilibrium pressure is negligible. The writer usually used the apparatus of Fig. 2.

## Experimental Results

Experimental results on the relation of the loading density and the equilibrium pressure over the temperature range 130° to 170° are shown in Figs. 1 and 4. At a given temperature the equilibrium pressure increases with the loading density. Table 1 gives the experimental equations which show the relation

Table 1

Experimental Equations for Equilibrium Pressure-Temperature Relation of the $CO_2$-$NH_3$-Urea-$H_2O$ System

| Loading density, g./cc. | Experimental equation $P$=atm., $T$=absolute temp. °K. |
|---|---|
| 0.20 | $\log P = \frac{-1960}{T} + 6.366$ |
| 0.40 | $\log P = \frac{-2139}{T} + 6.825$ |
| 0.60 | $\log P = \frac{-2237}{T} + 7.117$ |
| 0.80 | $\log P = \frac{-2369}{T} + 7.503$ |
| 1.00 | $\log P = \frac{-2444}{T} + 7.781$ |

Table 2

Extrapolated Values of Equilibrium Pressure at 180°, 200° and 250°C.

| Loading density, g./cc. | Equilibrium pressure, atm. 180°C. | 200°C. | 250°C. |
|---|---|---|---|
| 0.20 | 109 | 167 | 415 |
| 0.40 | 127 | 201 | 543 |
| 0.60 | 151 | 244 | 692 |
| 0.80 | 188 | 313 | 940 |
| 1.00 | 243 | 411 | 1280 |

between the temperature and the equilibrium pressure. Extrapolated values which were calculated at 180°, 200° and 250° from these equations are given in Table 2.

## Discussion of Results

Matignon and Frējacques[1] concluded already in 1920 that the system was bivariant, observing that the system consists of a vapor phase and a single homogeneous liquid phase, and assuming the following five reactions in the system.

$$CO(NH_2)(ONH_4) \rightleftarrows CO(NH_2)_2 + H_2O \quad (1)$$

$$CO(NH_2)(ONH_4) \rightleftarrows CO_2 + 2NH_3 \quad (2)$$

$$CO(NH_2)(ONH_4) + H_2O \rightleftarrows CO_3(NH_4)_2 \quad (3)$$

$$CO_3(NH_4)_2 \rightleftarrows CO_3H(NH_4) + NH_3 \quad (4)$$

$$CO_3H(NH_4) \rightleftarrows CO_2 + H_2O + NH_3 \quad (5)$$

They conjectured that the equilibrium pressure was a function of ratio of volume of the reaction vessel to initial content of carbamate in it at a given temperature.

Nevertheless, they could not only show these facts in their own experiments, but also their explanation that the system is bivariant is a mistake because the equation (5) is deduced from the other equations (2), (3) and (4).

In general, diversity of equilibrium pressure is a character proper to "the thermal dissociation compounds" such as $CO_2$-$NH_3$-$H_2O$ system.[6]

Supposing an equilibrium system of the thermal dissociation compound is charged in a sealed vessel with changeable volume by the movement of a piston, an isothermal increase of the volume induces the vaporisation of a part of the liquid phase. And if the volume decreases isothermally, a part of the vapor is condensed. In both cases, the total pressure of the system and the compositions of the liquid and gas phases undergo some change, although the total composition of the system remains as it is.

For example, pure water has a constant vapor pressure at a given temperature. If the water vapor decomposes into hydrogen and oxygen as the following equation at the temperature below the critical point,

$$2H_2O \rightleftarrows 2H_2 + O_2$$

hydrogen and oxygen would respectively dissolve into the liquid water with different solubility. Therefore, mol ratio of oxygen to hydrogen in the gas phase is not one by two and it will depend upon a ratio of initial content of water to volume of the vessel. At the same time the vapor pressure is indefinite and it will depend upon weight-volume ratio at the temperature.

By the above-mentioned qualitative explanation we can understand the diversity of the equilibrium pressure. In this paper the experimental results under the condition that

(6) "Gmelins Handbuch der Anorganischen Chemie," **23**, Ammonium, p. 327, Verlag Chemie, G.m.b. H., Berlin, 1936.

loading mol ratio of carbon dioxide to ammonia is one by two have been described. In the next papers the writer will intend to report on the equilibrium pressure under such condition as loading mol ratio is less than one by two, that is, loading ammonia is in excess to carbon dioxide and the compositions of the liquid and gas phases quantitatively measured at various conditions of the loading density and the equilbrium pressure.

## Summary

(1) In the study of the equilibrium pressure of the $CO_2$-$NH_3$-Urea-$H_2O$ system, it was experimentally found that the equilibrium pressure of the system is a function of loading density of reactants in the reaction vessel at a given temperature.

(2) The experimental equations that show the relation between temperature and equilibrium pressure were studied at various loading densities, under conditions that loading mol ratio of carbon dioxide to ammonia was one by two, and at the temperature range 130° to 170°.

(3) It was verified that the diversity of the equilibrium pressure of the system is reasonable.

The writer wishes to express appreciation for the kind guidance and the advice received from Prof. Shinjiro Kodama of Kyoto University and for the encouragement received from Dr. Kenji Fujimura, the chief of the Research Department, throughout this work.

*Research Department, Niihama Works,*
*Nissin Chemical Co., Ltd., Niihama*

# The Iodometric Determination of Propargyl Alcohol

By Kazumi YAMAMOTO, Minoru YOSHIMURA and Manzo TANAKA

(Received January 19, 1951)

## Introduction

Our studies were conducted to estimate the quantities of propargyl alcohol in the reaction products which are formed by the reaction of formaldehyde and acetylene in accordance with the so-called "Reppe's alkynol synthesis".

As propargyl alcohol has the active methyne group, some of the well known analytical methods for the acetylenic compounds were employed. They did not give any satisfactory results, presumably either for the reason of the method itself being imperfect or by the interfering action of formaldehyde which usually remains in the product.

Our new method gave good results, especially, in the presence of formaldehyde too.

**The Outline of the Several Methods Already Known:**—(A) Argentometry of propargyl alcohol is not suitable in the case when formaldehyde is present as indicated by Hanna and Sigga.[1]

(B) The methods[2,3] in which propargyl alcohol is precipitated as Cu-compound and then determined indirectly, are also not suitable, because the Cu-compound of propargyl alcohol precipitated with Ilosvay's reagent[4] is not merely $Cu-C\equiv C-CH_2OH$ but the mixture with $Cu(C\equiv C-CH_2OH)_2$, in proportion to the quantities of the reagent added.

(C) Potassium mercuric iodide method.[1] This method was recently proposed by Hanna and Sigga and gave good result for pure propargyl alcohol. The determination of propargyl alcohol is based on the following reaction.

$$2CH\equiv C-CH_2OH+K_2HgI_4+2NaOH$$
$$=(OH-CH_2-C\equiv C)_2Hg+2KI+2NaI+2H_2O$$

We have observed, however, that this method is not applicable too, in the presence of formaldehyde of more than 0.5%.

According to our experiments, the reaction between formaldehyde and potassium mercuric iodide is expressed as follows:—

$$K_2HgI_4+CH_2O+3NaOH$$
$$=2KI+HCOONa+Hg+2H_2O+2NaI$$

(1) Hanna and Sigga, *Anal. Chem.*, **21**, 1469 (1949).
(2) Hein and Meyer, *Z. Anal. Chem.*, **72**, 30 (1927).
(3) Willstätter, *Ber.*, **53**, 936 (1920).
(4) Ilosvay, *Ber.*, **32**, 2397 (1910).

In case both propargyl alcohol and formaldehyde are present, however, the stoichiometric relation between formaldehyde and potassium mercuric iodide indicates considerable deviation.

## Our New Method

We observed that one mole of propargyl alcohol reacts with one mole of iodine quantitatively in alkaline solution and this reaction proceeds as follows:—

$$HC{\equiv}C{-}CH_2OH + I_2 + NaOH = IC{\equiv}C{-}CH_2OH^{(5)} + NaI + H_2O$$

So, the excess of iodine may be backtitrated with standard thiosulfate solution after acidification. The result obtained has agreed well with the one by Hanna's method as shown in the following tables.

If the sample contains formaldehyde, which also reacts with iodine quantitatively as already known, the quantity of propargyl alcohol can be calculated by subtracting the amount of iodine corresponding to formaldehyde from the total of iodine consumed. The former is calculated from the quantity of hydrochloric acid determined in oximmetry of formaldehyde in another run of the same sample.

$$CH_2O + NH_2OH\text{-}HCl = CH_2NOH + H_2O + HCl$$

$$CH_2O + I_2 + 3NaOH = HCOONa + 2NaI + H_2O$$

**Reagents to be used:—**
*ca.* 1*N* Sodium hydroxide solution,
*ca.* 1*N* Sulfuric acid solution.
*ca.* *N*/10 Iodine solution,
*N*/10 Sodium thiosulfate solution,
*ca.* *N*/10 Hydroxylamine hydrochloride solution,
*N*/10 Sodium hydroxide solution

**Indicators:**—Starch solution, Methyl orange.

**Procedure of analysis:**—The sample containing 0.02 to 0.06 g. of propargyl alcohol is accurately taken and diluted to 10 cc. with water in conical beaker of 300 cc. capacity, then pipetted in by shaking 25 cc. of *N* NaOH solution and 25 cc. of *N*/10 iodine.

After letting it stand for about 10 minutes, 35 cc. of *N* sulfuric acid is added, thus liberated excessive iodine is titrated with *N*/10 sodium thiosulfate as usual. Let us assume the volume of thiosulfate required as $a$ cc.

Separately, blank run is held. Let us assume the volume of thiosulfate required in the blank run as $b$ cc.

So the quantity of propargyl alcohol (P.A.) is calculated as follows:—

$$\text{P. A.} = 0.005606\ \text{g.} \times \frac{b-a}{2}. \qquad (1)$$

In case when formaldehyde is present, first, $(b-a)$ cc. of thiosulfate is determined as above. Using the same sample the quantity of formaldehyde is separately determined with hydroxylamine hydrochloride as usual.

Let us, then, assume the volume of *N*/10 sodium hydroxide required for neutralizing hydrochloric acid liberated, as $c$ cc. So the quantity of propargyl alcohol is calculated as follows:—

$$\text{P. A.} = 0.005606\ \text{g.} \times \frac{(b-a)-2c}{2} \qquad (2)$$

The results obtained are shown in Tables 1 and 2.

Table 1

Result of Analysis of Pure Propargyl Alcohol

| P. A. weighed, g. | Our method calculated by Eq. (1), g. | Hanna's method, g. |
|---|---|---|
| 0.1018 | 0.1016 | 0.1014 |
| 0.05070 | 0.0506 | 0.05063 |
| 0.01018 | 0.01015 | 0.01014 |

Table 2

Result of Analysis of P. A. Containing $CH_2O$

| Sample weighed | | $CH_2O$ by oximmetry, g. | P. A. calculated by Eq. (2), g. |
|---|---|---|---|
| P. A. | 0.06198 | | 0.06199 |
| $CH_2O$* | 0.0018 | 0.0018 | |
| P. A. | 0.06198 | | 0.06196 |
| $CH_2O$* | 0.0180 | 0.0180 | |
| P. A. | 0.06198 | | 0.06200 |
| $CH_2O$* | 0.1703 | 0.1702 | |

* These values are determined by usual iodometry.
P.A. and $CH_2O$ were weighed separately and mixed before determination.

We have applied this method to the determination of methyl-(2)-butyne-(3)-ol-(2) which is prepared from acetylene and acetone, as well.

The result obtained was as follows:—

| Sample taken | Our method | Hanna's method |
|---|---|---|
| 0.05312 g. | 0.05310 g. | 0.05299 g. |

**Remarks:**—Our method indicates some deviation in result if the amount of formaldehyde exceeds three times of the amount of propargyl alcohol.

The effect of butyne-(2)-diol-(1.4) on the result is negligible. If the concentration of the sample and reagents are too high or the temperature is much higher than room temperature, the

(5) We synthesized this compound in the same reaction and identified.

result obtained often indicates high value which is due to the formation of 3,3,2-triiodo allyl alcohol.

$$HO\text{-}CH_2C{\equiv}CH+2I_2+NaOH = HOCH_2CI{=}CI_2+NaI+H_2O$$

This method suggests that it can be applied to the determination of the acetylenic derivatives of type of $RC{\equiv}CH$.

### Conclusions

(1) It is impossible to determine propargyl alcohol in the reaction products which are formed by the reaction of acetylene and formaldehyde, by the already known methods.

(2) In order to determine propargyl alcohol under such conditions we invented new analytical method which is based on iodometry of propargyl alcohol.

Our study was conducted under the guidance of and with the encouragement from Dr. K. Yoshikawa, and we were given instructive advice by Dr. S. Murahashi, Prof. of Osaka University, as to the mechanism of the reaction between propargyl alcohol and iodine. Upon taking this opportunity we wish to extend our thanks to them.

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*Omuta, Fukuoka*

# Concentration of $N^{15}$ by Chemical Exchange Reaction Method

Asao SUGIMOTO, Ryohei NAKANE and Tsunao WATANABE

(Received January 31, 1951)

### Introduction

For the purpose of the utilization of concentrated $N^{15}$ as tracer works, we have been studying the concentration of $N^{15}$ during these three years, and we are now able to concentrate the heavy nitrogen isotope up to nearly 10 atomic percent. The experimental results will be reported here briefly.

The method of the concentration of $N^{15}$ was quite the same as that of Urey and others,[1] namely the chemical exchange reaction between ammonia gas and ammonium ion in the packed concentrating column.

### Experimental Apparatus

The experimental apparatus consisted of two stages and their configurations were as shown in Fig. 1. The principal parts of the apparatus were as follows:

(1) **Concentrating column.**—The concentrating columns used in this work were made of glass tubes and total heights and inner diameters of the columns were 8 m. and 2.2 cm. for the 1st stage respectively and 6 m. and 1.0 cm. for the 2nd stage.

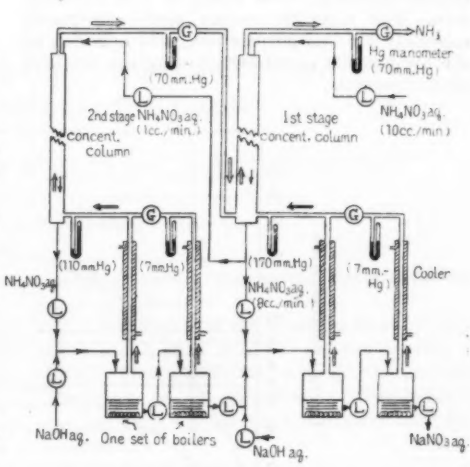


Fig. 1.
L: Liquid Pump. G: Gas Pump.

Each column was packed with the following; Fenske type (one turn helix) made of thin aluminum wire (0.3 mm. in diameter). The diameters of the helixes were 2.4 mm for the case of the 1st stage and 2.0 mm. for the case of the 2nd stage.

They were cleaned and boiled in water solution of $Na_2CO_3$. By this treatment, the surfaces of them were changed to gamma crystals

(1) H. C. Urey, J. R. Huffman, H. G. Thode and M. Fox, *J. Chem. Phys.*, **5**, 856 (1937); H. G. Thode and H. C. Urey, *J. Chem. Phys.*, **7**, 34 (1939).

of $Al_2O_3$.(2) These packing materials proved to be very satisfactory for the concentrating work as they were easy to produce on a large scale and also quite safe for the corrosion by the water solution of $NH_4NO_3$ and ammonia gas.

The space factors of the packing materials in the columns were 16.7% for the 1st stage column and 19.2% for the 2nd one.

(2) **Boilers.**—For each stage two sets of boilers were used. Each set was composed of five boilers made of copper tubes 10 cm. in diameter, four of which were 50 cm. in length and were placed horizontally while one was 20 cm. in height and was placed vertically. The five boilers were connected in series, the vertical one being placed at the end. Each boiler was heated with a 400 watt alumica heater. Water vapour was removed from the flow of ammonia gas at cold traps placed before each gas pump. The outsides of traps were cooled by methylalcohol-water mixture of about −15° circulatiug from a tank of a methylchloride refrigerating machine by a circulating pump. By introducing an auxiliary gas pump between two sets of boilers of each stage, we could reduce the residual amount of ammonium ions in the solution of $NaNO_3$ which would be drained from the last boiler of the stage less than one hundred thousandth (1/100,000) of the initial amount fed at the top of the column.

To keep the liquid levels in the boilers constant, we attached to the last boiler of each set a liquid level regulator as shown in Fig. 2. The liquid-contact electrodes were made of thin platinum foils. The magnetic valves were constructed especially for this purpose and were operated by the compression of rubber tubes by the action of electromagnets.

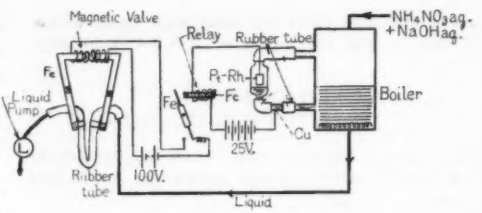


Fig. 2.

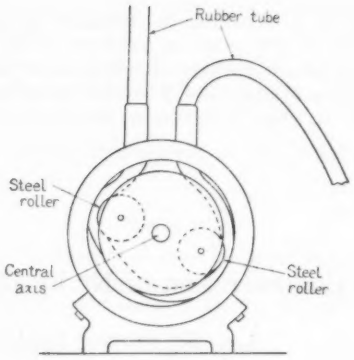


Fig. 3.

(3) **Liquid pump.**—For the transport of the chemical solutions ($NH_4NO_3$, NaCH, $NaNO_3$), we constructed a special type of liquid pump, the working mechanism of which can be easily seen in Fig. 3. By changing the velocity of rotation

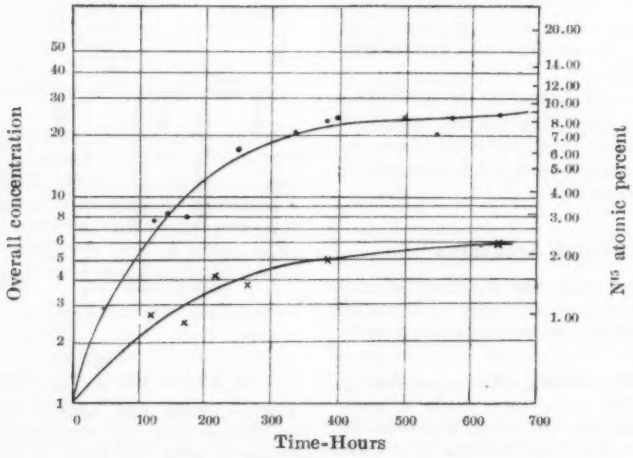


Fig. 4.—●, Concn. at the bottom of the second stage column; ×, Concn. at the bottom of the first stage column.

(2) We are greatly indebted to Miyata Laboratory of this institute for this surface treatment of the packing materials.

of the central axis, and inner diameter of the rubber tube, we could change the speed of the transport of liquid from 0.01 cc./min. to 30 cc./min. by a single pump. As for the lubricant between the steel rollers and the rubber tube, we used glycerine which proved to be very satisfactory.

(4) **Chemicals.**—As for the solution of the ammonium ion we used 60% solution of $NH_4NO_3$, to which 1% of methylalcohol was added. The feeding velocities of the ammonium nitrate solution were 10 cc./min. for the 1st column and 1 cc./min. for the 2nd column. As for the solution of NaOH, 30% solution of commercial caustic soda was used.

## Experimental Results

We had operated the apparatus mentioned above from June 21 to July 19, nearly 670 hrs. The pressure at the top of the column of each stage was kept at 70 mm. Hg and the pressure drops in the columns were 10 mm. Hg per meter for 1st stage and 6 mm. Hg per meter for the 2nd one.

The changing rate of the concentration of $N^{15}$ at the bottom of the column of each stage was shown in Fig. 4. From 420 hrs. we began to produce samples of concentrated $N^{15}$ in the form of $(NH_4)_2SO_4$ by sending bubbles of ammonia gas from the bottom of the 2nd stage column through $H_2SO_4$. Thus we could get totally 20 g. of $(NH_4)_2SO_4$ during this work. The $N^{15}$ contents of the samples varied from 8 to 9.3 atomic percent. The overall concentration factor of the two stages was 27 and that of the 1st stage only was 5.9.

In conclusion we express our thanks to the late Dr. Yoshio Nishina, the President of this Institute, for his kind encouragement throughout this work. We are also greatly indebted to the Ministry of Agriculture and Forestry for grants without which this work could not have been accomplished. We also wish to thank Messrs. Sadao Matsuo, Shyohei Isomura, Ryuzo Shibata, Shohichi Motonaga, Kozo Morishita for their assistance in connection with this experiment.

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# Adsorption of Proteins from Aqueous Solution on the Films of Stearate and Lipids[1]

By Taro TACHIBANA,[2] Kiyoshige FUKUDA and Kozo HAMAGUCHI[3]

(Received March 20, 1951)

A metal slide covered with a barium stearate multilayer film, which was rendered hydrophilic by treating with thorium nitrate solution, is highly polar and can adsorb proteins from their solution. A slide prepared in this way is dipped into a protein solution. The following washing and drying bring an increase in thickness which can be measured optically. We have studied, by such a procedure,[4] the adsorption of proteins. Some interesting phenomena observed in the investigation are briefly described below. The detailed description may be given elsewhere.

1. Adsorption of egg albumin from its aqueous solution was studied on the surface of stearate film conditioned with thorium nitrate. The effect of concentration of the solution and the time alloted for adsorption have been measured.

Preliminary experiments have led to the results that the adsorption was completed within five minutes at room temperature and the maximum thickness was 50 Å. which was deposited from the aqueous solution of the concentration over 0.01 percent. The adsorption was irreversible.

As far as the stearate film was left dipping in solution, the thickness of adsorbed layer never exceeded 50 Å. However, after taking

(1) Read before the Special Meeting of the Chemical Society of Japan, Tokyo on Nov. 11 th, 1949.
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(3) Present address, The Institute of Scientific and Industrial Research, Osaka University, Sakai, Osaka.
(4) I. Langmuir and V. J. Schaefer, *J. Am. Chem. Soc.*, **59**, 1406, 1672 (1937).

out the film from solution with the following washing and drying, the second dipping permitted the further increase of the thickness of adsorbed layer though the rate was much slower than in the case of the first dipping, *i. e.*, the increment was about 10 Å. thick at one hour after the beginning of the second adsorption. Thus, the repetition of dipping and drying always enhanced the adsorption. This seems to indicate that drying caused a certain change in the structure of adsorbed layer. Adsorbed layer of protein was found to decrease in thickness by bringing contact with 8 molal solution of urea. For instance, by this treatment the adsorbed layer decreased from 44 to 22 Å. in thickness for 16 hours, where it attained at minimal thickness.

By the way, it may be noted that the adsorption of egg albumin on unconditioned surface produced 20 Å. thick for 24 hours at 0°.

2. Likewise, experiments were performed with horse serum proteins. As shown in Table 1, it resulted that serum albumin was adsorbed on hydrophilic surface alone, while serum globulin was equally adsorbed from saline solution on both hydrophilic and hydrophobic surfaces. Serum globulin was not fractionated, so that which of the fractions was responsible for the phenomena was not established. Table 1 shows that salt also suppresses the adsorption of serum albumin.

3. A peculiar phenomenon was observed in dipping a slide having stearate multilayer film into rabbit serum. The maximal thickness of adsorbed layer, 50 Å., was obtained on the conditioned surface of stearate film, whereas with unconditioned stearate film the decrease of thickness of stearate film occurred at the rate of 15 Å. per one hour. This may be a case of solubilization and suggest a method of measuring the solubilizing power of serum towards a fatty acid.

Table 1

Adsorption of Horse Serum Protein from Solution onto Barium Stearate Film Conditioned or not with Thorium Nitrate.

| Protein solution | The thickness of adsorbed layer on | |
|---|---|---|
| | Conditioned surface, Å. | Unconditioned surface, Å. |
| Serum albumin in aq. solution, 0.5% | 36 | 5 |
| Serum albumin in physiologically saline solution, 0.5% | 28 | 0 |
| Serum globulin in physiologically saline solution. 1.5% | 68 | 71 |

Each figure represents an average of several determinations. Error is within 3Å.

4. Furthermore, experiments were made of the adsorption of serum protein on a single monolayer of lipids[5] transferred onto conditioned stearate film at compression of 15 dynes. Such a slide was dipped into human serum for ten minutes at 10°. The adsorption produced the thickness of 50-60 Å. on cardiolipin monolayer, 25-35 Å. on lecithin monolayer. These results may indicate the adsorptive power of respective lipids to serum portein.

The authors express their sincere thanks to Prof. Jitsusaburo Sameshima for his kind advice and encouragement. The expense of this work has been defrayed from the Scientific Research Encouragement Grant from the Ministry of Education.

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(5) Samples were kindly provided by Department of Serology, Faculty of Medicine, the University of Tokyo.

# Some Higher Alkyl Naphthenates as Lubricating Oil for Fine Instruments

By Tsutomu KUWATA,[1] Shizuo NOGUCHI[2] and Hiroyasu ANDO[2]

(Received April 20, 1951)

Lower alkyl naphthenates, such as methyl or ethyl esters, have been known in detail, but as to the esters of higher fatty alcohols having more than eight carbon atoms no description has been found in the literature.

The present authors synthesized several higher alkyl esters of naphthenic acids and found that these new esters have suitable properties as lubricating oil for several fine instruments.

## Synthesis of Higher Alkyl Naphthenates

Higher fatty alcohols used in the experiment are listed in Table 1. Refined naphthenic acids free from neutral oils, phenols, and other impurities are used for the study of characteristic properties of esters, and crude naphthenic acids contaminated with neutral oils, phenols, resinous substances and other impurities are employed for the estimation of commercial qualities of esters.

**1.** Refined naphthenic acids ($R_I COOH$) derived from Niitu light machine oil distillates are light yellowish viscous liquid and have the following properties: b. p. 180-225°/9 mm.Hg (uncor.); $d_4^{15}$ 1.0025; $n_D^{15}$ 1.4896; acid value 223.6; av. mol. wt. calcd. 250.9.

**2.** Refined naphthenic acids ($R_{II}COOH$) produced in the refining of the same distillates are yellowish viscous liquid and have the following properties: b. p. 182-229°/9 mm.Hg (uncor.); $d_4^{20}$ 0.9992; acid value 220.6; av. mol. wt. calcd. 254.3.

**3.** Crude naphthenic acids ($R_{III}COOH$) obtained by the distillation of the crude petroleum acids imported from abroad have approximately the following composition: Pure naphthenic acids (acid value, 227.1) 76%; phenols, neutral oils and other impurities 23%. The acids are brownish viscous liquid and have the following properties: b. p. 155-247°/9 mm.Hg (uncor.); $d_4^{20}$ 0.9882; $n_D^{20}$ 1.4957; acid value 192.6. Higher fractions (above 200°/5 mm.Hg) of the neutral oils contained

Table 1

Properties of Higher Fatty Alcohols Used

| Alcohols | Materials | B. p. °C. (mm.Hg uncor.) | $d_4^{20}$ | $n_D^{20}$ | Hydroxyl value | Remarks |
|---|---|---|---|---|---|---|
| 2-Ethylhexyl alcohol | Synthetic | 182-183 | 0.8346 | 1.4316 | — | — |
| *n*-Octyl alcohol | Reduction of coconut oil | 191-196 | 0.8225 | 1.4298 | 429.8 | B. p. (mainly) 193° |
| Decyl alcohol | | 120-125 (15) | 0.8299 | 1.4356 | 353.8 | B. p. (mainly) 122-123°/15 mm.Hg |
| Lauryl alcohol | | 143-148 (15) | — | — | 295.0 | M. p. 23.5-25.5° |
| Lauryl alcohol (industrial) | | 130-165 (15) | 0.8273 | 1.4377 | 224.2 | Solid. point 5.5°; Purity calcd. from H. V. 74.5% |
| Cetyl alcohol | Spermaceti | 188-190 (15) | — | — | 233.0 | M. p. 49.0-50.5° |
| Oleyl alcohol | Sperm liquid alcohol | 205-210 (13) | 0.8505 | 1.4630 | 209.8 | Iodine value 91.5 |
| Sperm alcohol | Sperm oil | 165-205 (13) | — | — | 214.6 | I.V. 45.2; av. mol. wt. calcd. from H. V. 261.4 |
| Sperm liquid alcohol | * | 80-260 (13) | 0.8495 | 1.4604 | 204.5 | I.V. 83.2; av. mol. wt. calcd. from H. V. 274.3 |

* Sperm liquid alcohol was prepared from sperm alcohol by separating the solidified substance in acetone solution at −3~−7°; yield, 45.5% of sperm alcohol.

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(2) Central Technical Laboratory, Nippon Oil Co., Ltd.

in the crude naphthenic acid amounted to 3.4% (in weight) and it is considered to be most probable that naphthenic esters prepared from the crude naphthenic acids contain the corresponding amount of hydrocarbon oil as impurity.

**Procedure.**—The mixture of higher fatty alcohols, excess naphthenic acids, moderate quantity of xylene and conc. sulfuric acid is boiled in a flask fitted with reflux condenser and accessary which is widely used for measuring the water content in organic substance. When the volume of water distilled is constant, reactions are considered to be completed. The reaction products are washed with 0.5 *N* sodium hydroxide and then with distilled water and dried over sodium sulfate. After removing the solvent, the reaction products are distilled under reduced pressure in the presence of 1% anhydrous sodium carbonate or no additive. The data obtained are given in Table 2.

From these it is notable that under these experimental conditions esterification of naphthenic acids is carried out with satisfactory result. In the purification of the esters it is desirable to distil them under pressure as low as possible in order to avoid the increase of acid value.

## General Properties of Higher Alkyl Naphthenates

The general properties of naphthenates are shown in Table 3. The increase of the carbon number of side chain attached to the carboxyl group reduces density, refractive index, and increases viscosity, and improves viscosity-temperature characteristics as evidenced by high value of kinematic viscosity index. The reaction of the esters is always neutral except those prepared from the crude naphthenic acids distilled with no additive. Corrosion test is good. Esters have the odor resembling to mineral oil, and not the characteristic unpleasant odor of naphthenic acids or lower alkyl naphthenates. The higher alkyl naphthenates are pale yellowish liquid, and the color of the oil may be greatly improved by the redistillation.

As may be seen from the fact that the esters prepared from crude naphthenic acids have properties as good as those from refined naphthenic acids, small amount of neutral oils included within the esters have no unfavourable influence upon the esters. But it is wiser to use crude naphthenic acids from kerosene or gas oil fractions as the starting materials, because the presence of high boiling neutral oil is apt to give dark color to the esters.

The data cited in table 3 indicate that the esters are mostly characterized by little change in viscosity with temperature, low viscosity and viscosity ratio, adequately low volatility, high flash point, and reliable resistance to heating. They spread on metal or glass surface far less extent than hydrocarbon oils. Though

Table 2

Synthesis of Higher Alkyl Naphthenates

| Names | Naphthenic acids: Symbol | Naphthenic acids: g. mol | Alcohols, g. mol | Xylene, cc. | $H_2SO_4$, g. | Reaction time, hrs. | Reaction products, g. | Distil.* method | Esters: B. p. (°C./5 mm.) | Esters: Main** (°C./5 mm.) | Esters: Obtained, g. | Yield, % to alcohols |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2-Ethylhexyl naphthenates | $R_{II}COOH$ | 0.39 | 0.3 | 350 | 7 | 2 | 95.0 | × | 200-240 | 200-220 | 84.3 | 77 |
| n-Octyl naphthenates | $R_{II}COOH$ | 0.39 | 0.3 | 350 | 7 | 2 | 93.0 | × | 200-245 | 210-230 | 83.5 | 76 |
| Decyl naphthenates | $R_{II}COOH$ | 0.26 | 0.2 | 250 | 5 | 2 | 72.1 | × | 200-255 | 220-240 | 63.4 | 81 |
| Lauryl naphthenates | $R_{II}COOH$ | 0.39 | 0.3 | 400 | 8 | 2.5 | 117.0 | 0 | 210-265 | 240-260 | 99.1 | 78 |
| Lauryl (industrial) naphthenates | $R_{III}COOH$ | 0.11 | 0.1 | 150 | 3 | 2 | 41.5 | × | 200-280 | 235-260 | 32.8 | 78 |
| Cetyl naphthenates | $R_ICOOH$ | 0.05 | 0.03 | 50 | 1 | 1.5 | 12.9 | 0 | 200-278 | 260-275 | 11.0 | 77 |
| Oleyl naphthenates | $R_ICOOH$ | 0.05 | 0.03 | 50 | 1 | 1.5 | 13.5 | 0 | 200-295 | 275-290 | 11.7 | 78 |
| Sperm naphthenates | $R_ICOOH$ | 0.05 | 0.03 | 50 | 1 | 1.5 | 13.6 | 0 | 200-291 | 270-290 | 11.4 | 77 |
| Sperm liquid naphthenates | $R_{III}COOH$ | (35.0) 0.10 | 0.1 | 150 | 3 | 4 | 45.9 | 0 | 200-300 | 285-300 | 34.9 | 69 |

* 0, No Additive; ×, in presenece of 1% anhydrous sodium carbonate.

** "Main" means the range of temperature in which more than 80% (in weight) of the esters are distilled.

Table 3

General Properties of Higher Alkyl Naphthenates

| Esters | Color (union) | $d_4^{25}$ | $n_D^{25}$ | Saponification number | Acid value: Non treating | Acid value: After heating | Iodine value | Solid. point, °C. | Flash. point,** °C. | Volatility,*** % | Heating†: Ppt. | Heating†: Color (union) | Kinematic viscosity (cst)††: Non treating 30°C. | 50°C. | 100°F. | 210°F. | Kinematic viscosity: After ht. 50°C. | Viscosity ratio (50°C.) | Kinematic viscosity index |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2-Ethylhexyl naphthenates | 1 | 0.9306 | 1.4745 | 140.5 | 1.1 | 1.1 | 0.5 | −47 | 196 | 0.017 | None | 3½ | 29.85 | 13.38 | 21.47 | 3.74 | 13.52 | 1.00 | 43 |
| *n*-Octyl naphthenates | 1½ | 0.9266 | 1.4721 | 144.8 | 0.9 | 1.2 | 0.8 | −52 | 198 | 0.026 | 〃 | 2½ | 21.82 | 10.70 | 16.14 | 3.44 | 10.79 | 1.00 | 95 |
| Decyl naphthenates | 1½ | 0.9205 | 1.4719 | 120.7 | 2.7 | 2.9 | 1.2 | −43 | 197 | 0.025 | 〃 | 2½-3 | 25.64 | 12.40 | 18.88 | 3.85 | 12.45 | 1.00 | 106 |
| Lauryl naphthenates | 1 | 0.9139 | 1.4707 | 113.2 | 0.3 | 0.9 | 1.0 | −45 | 210 | 0.012 | 〃 | 2-2½ | 30.15 | 14.15 | 23.36 | 4.53 | 15.15 | 1.07 | 122 |
| Lauryl (industrial)* naphthenates | 1½ | 0.9152 | 1.4747 | 111.8 | 0.0 | <0.1 | 2.9 | −45 | 207 | 0.028 | 〃 | 2½-3 | 31.92 | 14.97 | 23.31 | 4.46 | 15.13 | 1.01 | 116 |
| Cetyl naphthenates | 1-1½ | 0.9077 | 1.4605 | 105.8 | 2.2 | 2.3 | 2.4 | −10 | 215 | 0.026 | 〃 | 1-½ | 42.36 | 17.65 | 30.49 | 5.66 | 20.46 | 1.11 | 136 |
| Oleyl naphthenates | 1½ | 0.9087 | 1.4653 | 100.5 | 2.7 | 2.8 | 36.6 | −40 | 193 | 0.016 | 〃 | 1½ | 45.38 | 21.11 | 32.84 | 6.10 | 22.78 | 1.03 | 138 |
| Sperm naphthenates | 1½-2 | 0.9071 | 1.4633 | 105.4 | 1.6 | 1.8 | 20.2 | −16 | 220 | 0.005 | 〃 | 1½-2 | 47.03 | 21.63 | 33.96 | 6.24 | 22.93 | 1.06 | 138 |
| Sperm liquid* naphthenates | 1½ | 0.9064 | 1.4733 | 100.9 | 0.0 | <0.1 | 41.9 | −32 | 198 | 0.023 | 〃 | 3 | 38.33 | 18.12 | 28.07 | 5.40 | 18.73 | 1.03 | 138 |

* The distillate was washed with alkali solution in order to remove the acidic substances produced by thermal decomposition of crude naphthenates.

** Determined with Pensky-Martens closed tester.

*** Per cent loss of weight in 5 hr. at 98° in a convection type oven.

† Observed after 6 hr. at 140° in a convection type oven.

†† Determined with modified type of Ostwald viscometer.

cetyl and sperm naphthenates have high solid points, esters of higher saturated alcohol having not more than twelve carbon atoms have low solid points below −40°. On comparing the two isomers, 2-ethylhexyl and *n*-octyl esters, the former has higher boiling point, higher viscosity, and smaller viscosity index than the latter. The higher solid point of the former may be accounted for low temperature viscosity relationship.

It seems unavoidable that acid value of the distillate slightly increases during distillation under pressure as low as 5mm. In order to obtain fractions of lower acid value it may be necessary to distil the esters under high vacuum as far as possible. The presence of small quantities of anhydrous sodium carbonate may decrease acid value, though not to a satisfactory extent.

Considering from these properties, the esters of naphthenic acids above mentioned are almost comparable in lubricating quality to the lubricants hitherto known with the exception of cetyl esters. Some esters, lauryl naphthenates may be expected to be available for the lubrication of watch, clock, and other delicate machinery of fine instruments.

## Conclusion

2-Ethylhexyl, *n*-octyl, decyl, lauryl, cetyl, oleyl and sperm esters of pure naphthenic acids and lauryl (industrial) and sperm liquid esters of crude naphthenic acids are synthesized.

As the result of experiments it was found that higher fatty alkyl esters of naphthenic acids possess the most excellent qualities as lubricating fluids for delicate machinery of fine instruments; *i. e.*, pale yellowish color, low viscosity, low evaporation rate, low solid point, high flash point, high kinematic viscosity index, high thermal stability, and slow spreading velocity on metal or on glass surface.

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# LETTER

## Synthesis of *p*-Acetylaminocinnamaldehyde Thiosemicarbazone

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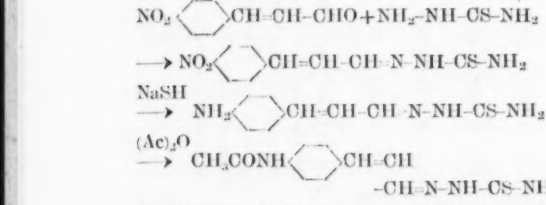
This paper reports the synthesis of a new antituberculous substance, *p*-acetylaminocinnamaldehyde thiosemicarbazone having activity in concentration of 1.3 γ/ml. (Aoyama B strain, Sauton medium). The reactions are given in the scheme:



A mixture of 8.9 g. of *p*-nitrocinnamaldehyde, 4.6 g. of thiosemicarbazide and 90 ml. of ethanol was heated by stirring on a steam bath for 20 minutes. After cooling, the solid product was filtered, washed with ethanol and dried, giving 11.9 g. (92%) of *p*-nitrocinnamaldehyde thiosemicarbazone (I), m. p. about 224° (decomp.). *Anal.* Calcd. for $C_{10}H_{10}O_2SN$: N, 22.38. Found: N, 22.24.

After saturation of a mixture of 20 ml. of ethanol and 8 ml. of 2 *N* aqueous sodium hydroxide solution with hydrogen sulfide, 2.5 g. of (I) was added to the mixture in one portion. This mixture was heated at 50° for ten minutes, while crystals began to separate. After heating for further three minutes at 75° and after cooling, crystals were filtered, washed first with ethanol, then with water and again with ethanol, giving 1.6 g. (73%) of *p*-aminocinnamaldehyde thiosemicarbazone (II), m. p. 207° (decomp.). *Anal.* Calcd. for $C_{10}H_{12}N_4S$: C, 54.53; H, 5.50. Found: C, 54.29; H, 5.27.

To 1.1 g. of (II) suspended in 50 ml. of ethanol was added 2 ml. of acetic anhydride and the mixture was stirred for five minutes. Crystals were filtered and washed with water, giving 2.5 g. (95%) of *p*-acetylaminocinnamaldehyde thiosemicarbazone (III), m. p. 225° (decomp.). *Anal.* Calcd. for $C_{12}H_{14}OSN_4$: C, 54.95; H, 5.38. Found: C, 54.89; H, 5.48.

The nitro and amino compounds (I and II) also proved to have antituberculous activity.

Biological evaluation of these substances was executed by Dr. T. Takebe. The author wishes to express his gratitude to Dr. T. Takebe for his favor.

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